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XXVI.—*On a Method of Measuring the Pressure of Light by Means of Thin Metal Foil. Part II.* By GILBERT D. WEST, B.Sc.

RECEIVED MAY 12, 1916.

IN an earlier Paper to the Physical Society* I have described the measurement of the pressure of light by a method requiring few of the elaborate precautions generally necessary in such experiments. The essential feature of the apparatus was a strip of gold leaf suspended in the middle of a test tube containing air or hydrogen at reduced pressure. Radiation from a 32 c.p. carbon filament lamp, impinging directly on one side of the strip, was sufficient to cause a microscopically measurable deflection of the end.

The pressure of normally incident radiation on a perfectly reflecting surface has been shown† to be numerically equal to twice the energy content of the radiation per unit volume, and hence if this quantity be measured in the way described below, a check on the original observations can be made. A mean of the results of several successive experiments with the deflected strips, gave a value for the pressure of radiation which only differed from that calculated from the energy density by a small per cent. The accuracy and constancy of the final results seemed to preclude their being seriously affected by gas action, but as gas action had to be taken into consideration, the present research was undertaken with a view to its fuller investigation, and if possible to its complete elimination.

As it is convenient to know in advance the value of the true pressure of the radiation employed, the measurements and calculations required for this purpose will be dealt with first.

Measurement of the Energy Density.

The method used was similar to that described in the previous Paper. The initial rate of rise of temperature of a blackened copper plate enclosed in the tube, was measured by means of an attached copper eureka thermo-junction. Due allowance was made for cooling corrections, and the lamp black was again

* "Proc. Phys. Soc.," Vol. XXV., 1913, p. 324.

† Maxwell, "Electricity and Magnetism," Vol. II. Larmor, "Encycl. Brit.: Radiation." See also Callendar, "Nature," Jan. 1, 1914.

assumed to absorb 95 per cent. of the incident radiation. The cold junction was immersed in oil contained in a vacuum flask, and during an experiment a delicate indicating thermometer in the oil, only showed negligible variations. The calibration of the thermo-junction was carried out in the usual way, and a number of minor matters received fuller consideration than was previously given.

When, from the measurements thus taken, the energy reaching 1 sq. cm. in one second is known, the energy per 1 c.c. can be calculated from a knowledge of the velocity of light.

The 32 c.p. lamp was enclosed in a metal box whose front face had been replaced by a glass screen covered with a few thin wires. Inasmuch as it is required that the radiation should be normally incident, the lamp was not brought too close to the tube—a calculation of the limiting approach having been previously made. The current passing through the lamp was kept at the same value throughout all the experiments.

The results obtained are indicated in the course of the ensuing work. Owing to extraneous thermo-electric effects, especially at brass contact screws*, the accuracy was not quite as great as had been hoped. Nevertheless on drawing a curve evenly between the points representing the energy density at various distances from the source, it was found that none of the readings diverged by more than about 3 per cent. This accuracy is above what is required.

Reflecting and Transmitting Powers of the Foils Used.

By coating the front surface of the copper plate of the apparatus described in the previous Paper, with the foil to be used instead of with lamp black, it was possible to obtain measurements of the fraction of the incident radiation that was absorbed. More satisfactory results, however, were obtained with an apparatus somewhat similar to that originally used by Lebedew.† The bulb of a sensitive thermometer was fitted into a hole in a small block of copper. Thermal contact was secured by means of a little mercury, and the whole was placed in the tube in which subsequent measurements were carried out. The front face of the block was first coated with lamp black and afterwards with the foil under observation, whilst

* A. G. Warren and F. Murphy, "Electrician," Jan. 31, 1908.

† Lebedew, "Ann. der Physik," VI, p. 433, 1901.

the rates of rise of temperature on exposure to radiation, were, in each case, measured by means of a magnifying cathetometer telescope.

By interposing a screen made of gold or aluminium foil, between the source and the blackened block, it was possible to show that neither kind of foil transmitted an appreciable fraction of the incident radiation. The only correction therefore in calculating the reflecting power of the foil, is the re-reflection* from the glass of the tube. This amounts to about 7 per cent. Re-reflections after the first need not be considered.

As a mean of several observations, it was found that both gold and aluminium foil reflected 90 per cent. of the incident radiation.

It was also found that light was reflected from a sheet of foil, in a direction sufficiently close to the normal for the purposes of the experiment.

Calculation of the Deflection of the Strip.

Since the foil reflects 90 per cent. of the incident radiation, and since 7 per cent. is re-reflected from the glass of the tube, the total pressure of the radiation is given by

$$E(1+0.07 \times 0.9)(1+0.9) \text{ or } 2.04E$$

where E is the energy density of the incident beam.

A certain amount of radiation, however, strikes the back of the glass tube, and some of this is reflected to the back of the strip. For a strip three-quarters the width of the tube, it is estimated that the normal component of this radiation is about 1 per cent. of all that is incident on the strip. It is therefore necessary to substitute $2.02E$ for $2.04E$.

It can be shown that a uniform flexible strip when deflected by a small uniform pressure, still remains straight. To a close degree of approximation, therefore, we may calculate the deflection of a strip such as that represented in Fig. 1, by taking moments about the axis of rotation.

It was considered preferable in this research to find, by means of a Bunge balance, the mass of 1 sq. cm. of the sheet of foil from which the strip was cut, rather than to weigh the strip itself, and we may modify the original formula accordingly.

* Re-reflection was not considered in the original Paper. I have to thank the late Prof. Poynting and Dr. Barlow for the suggestion.

If we write h the distance of the centre of gravity of the strip below the axis of rotation AB as $\frac{l^2+f^2}{2(l+f)}$, where f is the length of the folded part AC , Fig. 1. We may write the deflection of the end of the strip of length l as

$$d = \frac{2.02El}{\left(1 + \frac{f^2}{l^2}\right)\rho g}$$

where ρ is the mass of 1 sq. cm. of the foil.

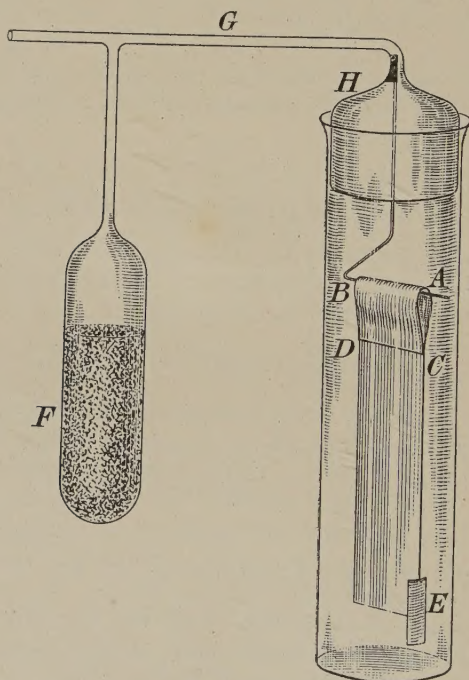


FIG. 1.

The Apparatus.

There are a few modifications of the original apparatus that need explanation. The top of the tube was closed by the hollow stopper H . In order to obtain a clear image of the end of the strip a small piece of cover glass was cemented to the inside of the tube at E by means of solid Canada Balsam. Another piece of cover glass was attached to the outside of the

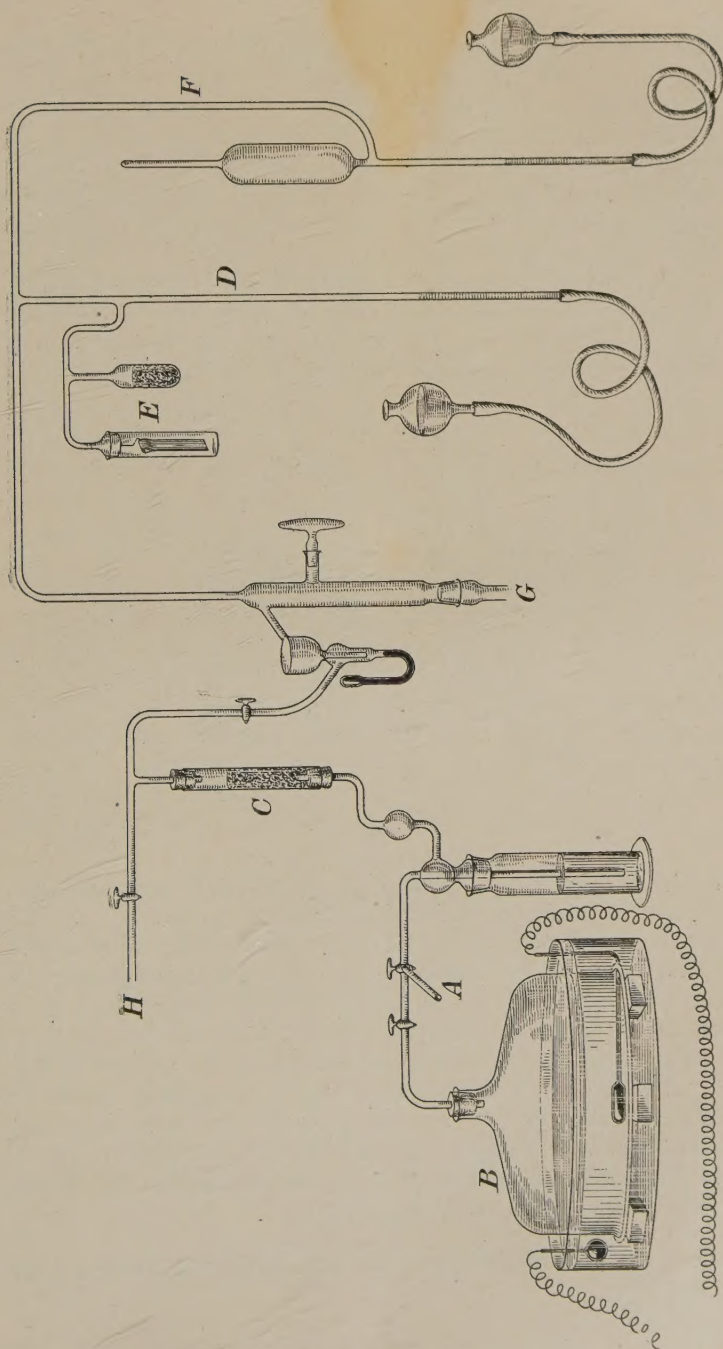


FIG. 2.

tube with a viscous solution of Canada Balsam in Xylol. By this means it was found possible to get improved definition of the image given by the microscope. When it was required to obtain very high vacua, a tube was attached similar to *F*, containing charcoal that had been prepared by very slowly calcining elder pith.* In the ordinary course of events, however, the tube *G* was connected directly to a motor-driven Gaede pump and a McLeod gauge.

The general arrangement of the apparatus is shown in Fig. 2. Air may be admitted to the pump at *A*, but by a turn of the cock, electrolytically generated hydrogen from the reservoir *B* may be admitted instead. Before entering the pump, the gas

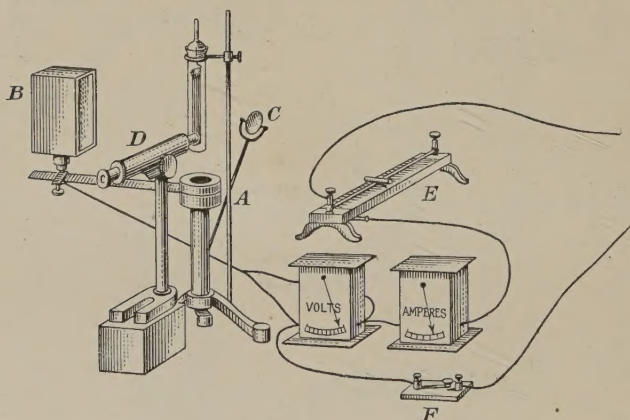


FIG. 3.

is forced to pass, first through strong sulphuric acid and then through a tube *C* containing phosphorous pentoxide. *D* is a barometric seal which prevents any small leakage to the tube *E* when the pump has ceased action. *F* is a McLeod gauge, *G* is directly connected to the Gaede mercury pump, and *H* is connected to a rotary pump exhausting to about 1 cm. mercury.

The apparatus for taking observations is represented in Fig. 3. The tube is mounted on a stand *A*, specially made by Messrs. Griffin & Co., and the lamp *B* can easily be swung round from side to side. Behind the tube is a small mirror *C* to illuminate the field of vision of the microscope *D*. *E* is a variable resistance, and *F* is a switch.

* In this connection I have to thank Dr. S. W. J. Smith for valuable suggestions.

A No. 3 Leitz objective coupled with a X20 eyepiece was used in the observing microscope. The slight chromatic aberration was reduced by means of a yellow screen placed in front of the eyepiece.* Before exhausting the tube, the stopper was sealed down with a mixture of wax and resin. The pump was probably capable of evacuating to pressures considerably below the vapour pressure of mercury,† but as no special precautions were taken, this was not generally attempted. For very low vacua, reliance was placed on liquid air and charcoal.

RESULTS.

Expansion of the Strips, due to Rise of Temperature.

Much light is thrown on the main issues, by a subsidiary phenomenon which escaped notice in the original Paper, owing probably to the bad definition of the image in the microscope, caused by the glass of the test tube.

The phenomenon referred to is the expansion of the strip under the influence of the radiation. To observe the expansions it was necessary to attach pieces of copper foil to the ends of the strips, as otherwise the movements under the influence of radiation prevented accurate observation. The expansion takes place rapidly, and is small and constant for gas pressures down to 1.5 cm. Below this it shows a slight increase, and then remains constant until a pressure of about 0.002 cm. is reached. On lowering the pressure still more it increases, until with the lowest vacua obtainable, it is nearly 20 times the original value. A series of results is given below.

ALUMINIUM STRIP.

Length=7.43 cm. Distance of lamp=10.5 cm. Energy density of radiation
= 1.95×10^{-5} ergs./cc.

Pressure.	Expansion of strip in air.
74.3 cm. of mercury (atmosphere)	0.5×10^{-3} cm.
41.3 cm.	0.5 " "
24.3 cm.	0.5 " "
5.0 cm.	0.5 " "
1.5 cm.	0.5 " "
0.35 cm.	0.6 " "
0.027 cm.	0.6 " "
0.0025 cm.	0.8 " "
0.0005 cm.	1.6 " "
0.0001 cm.	2.4 " "
Liquid air vacuum.	8.7 " "

* I am indebted to Dr. Salisbury, of East London College, for this suggestion.

† "Gaede Sci. Abs.," p. 471, 1915; also "Ann. der Physik," 46, p. 357, 1915.

When the apparatus was filled with hydrogen (whose thermal conductivity is six times that of air), the expansions for pressures down to 0.005 cm. were scarcely observable, being about 0.1×10^{-3} cm. They increased after that point however.

The rises of temperature that the expansions of the strips imply, are shown in the table below. The values assumed for the co-efficients of expansion of aluminium and gold are 25.5×10^{-6} , and 13.9×10^{-6} , respectively.*

Pressures.	Rise of temperature (Degrees Centigrade).			
	Aluminium strip.		Gold strip.	
	In air.	In hydrogen.	In air.	In hydrogen.
74.3 cm.	2.5	Hardly observ- able, about 0.5	1.8	Too small to be observed
Liquid air vacuum	46.0	...	44.5	...

The estimated difference of temperature of the two sides of the aluminium and gold strips respectively, was $6 \times 10^{-7}^{\circ}\text{C.}$, and $9 \times 10^{-8}^{\circ}\text{C.}$ No effects attributable to these small differences of temperature have yet been observed.

The results are almost self explanatory. Convection, conduction and radiation each play a part in determining the temperature of the strip at pressures down to about 1 cm. Conduction is independent of pressure unless this is very low, and, together with radiation, is the important factor until the very lowest pressures are reached, at which radiation alone is important. Thus at high pressures the rise of temperature is small, but at very low pressures it is considerable. The results obtained are in general agreement with those of Kundt and Warburg,† and they are in close agreement with the more precise results of Sir William Crookes.‡

The accepted view that convection is unimportant at pressures below 1 cm. is confirmed, and in the work shortly to be described, it will be found that satisfactory explanations of phenomena can be given by neglecting convection, at low pressures, altogether.

The Thermo-Kinetic Reaction.

The motion of the strip under the influence of radiation was considered in the previous Paper down to a pressure of about

* Voigt, 1893.

† "Pogg. Ann.," CLVI., p. 177, 1875; also "Phil. Mag.," July, 1875.

‡ "Proc. Royal Soc.," Vol. XXXI., p. 239, 1880-81.

1 cm. At that pressure, only very small gas action effects make their appearance, but as the pressure is lowered to, say, 0.002 cm., the movements of the strip may become a hundred times as large as before.

The strip may move initially either towards or from the source, and the first movement is followed by a much slower movement which is always away from the source. The first movement is strongest when the tube is inclined to the vertical—that is to say, when the end of the strip is nearer to one side of the tube than to the other. A typical series of readings for various pressures is given below in the table and in the diagrams on following page. It will be noted that in spite of the inclination of the tube, reasonable values for the pressure of light are obtained both at 1.5 cm. and 0.9 cm. of mercury.

ALUMINIUM STRIP.

Length=7.43 cm. Distance of lamp=10.5 cm. Energy density of radiation= 1.95×10^{-5} ergs./c.c. Tube inclined so that end of strip was nearer to right side of tube. Observations taken at the end of the first movement.

Pressure.	Deflections.		Mean deflection from lamp.	Deflection calculated from energy density.
	Lamp on left side.	Lamp on right side.		
1.5 cm. Hg.	0.3×10^{-3} cm.	6.6×10^{-3} cm.	3.1×10^{-3} cm.	2.6×10^{-3} cm.
0.9 cm. Hg.	towards lamp 1.6	from lamp 7.9	3.1	2.6

When the tube was inclined in the opposite way, so that the end of the strip was nearer to the left side than to the right, a similar series of curves, as given on following page, was obtained, but the initial deflections were to the right instead of to the left. When the tube was filled with hydrogen, and when the aluminium leaf was exchanged for one of gold, similar curves were again obtained. The material of the strip and the nature of the gas seemed to have little influence on the results.

As shown by the curves the slow progressive movement that occurs when the first movement is over, is always away from the source, and it is therefore natural to attribute this motion to the gradual warming up of the surface of the tube. Further, it is possible to reduce greatly the ratio of the rate of this motion to the deflection, by the interposition of a thick glass plate in the path of the radiation. At low pressures, when the mean free path is a few centimetres, we may consider the strip

to be bombarded by molecules returning from the heated glass surface. The strip is therefore deflected in the way observed. As the surface of the glass still remains hot when the lamp is switched off, and as the bombardment therefore continues, the strip does not return to zero for some time.

As was observed in the expansion experiments, the heating of the strip takes place rapidly, and it is this heating of the strip that accounts for the first part of the curves.

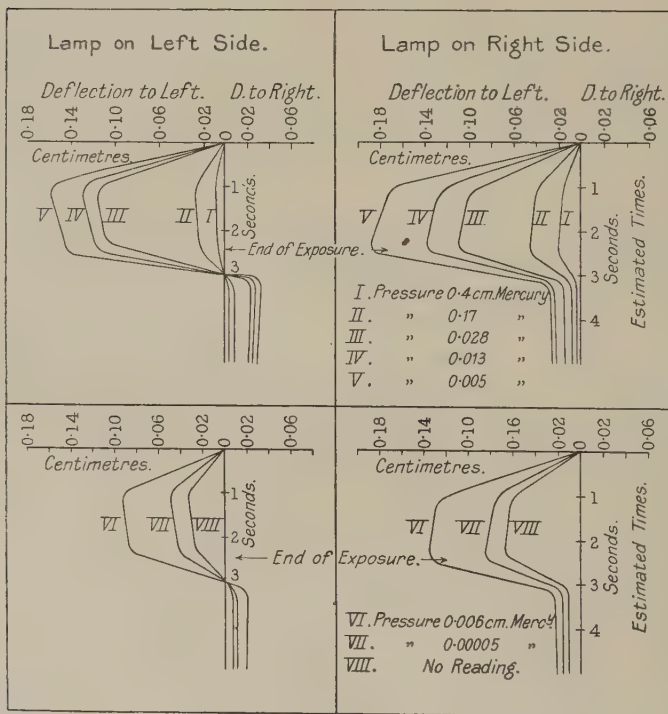


FIG. 4.

Molecules that strike the strip are sent back with increased velocities, and, at very low pressures, a given molecule strikes the side of the strip nearest the glass more frequently than does the corresponding molecule on the other side. A greater change of momentum per second implies a greater pressure, and hence motion of the strip. As the pressure rises and the mean free path is reduced, molecular collisions complicate the problem, and the simple theory needs the same elaborate

modification that was given by Prof. Osborne-Reynolds* in connection with the theory of the Crookes Radiometer.

The deflections of the strips due to the heated glass rendered the apparatus unsuitable for the observation of the pressure at which the gas action effect described above reached a maximum, and recourse was therefore had to the weighted gold and aluminium strips used in the expansion experiments. It was found that throughout the region of pressures 0.01 cm.—0.0005 cm. there were no great variations. The maximum in hydrogen was much the same as in air. To be certain of any difference, more precise experiments would be required. The results are similar to those of Sir William Crookes,† although the conditions are somewhat different. A comparison is given in the table below.

GOLD STRIP.

Pressure.	Deflections obtained.	Magnitude of radiometer effect calculated from Crookes' results.
0.16 cm. mercury	0.1 eyepiece divisions	1.0
0.02 "	0.4 " "	3.9
0.002 "	0.55 " "	8.3
0.0005 "	0.50 " "	4.1
0.0001 "	0.40 " "	2.0
0.00005(?) "	0.35 " "	1.7

To confirm the above theory a strip was mounted in a small rectangular glass cell in such a way that by tapping the cell the strip could be moved from side to side. The apparatus is represented in Fig. 5. The radiation may be allowed to fall normally on either side of the strip, but the deflection is always away from the closest glass surface, and is easily visible to the naked eye when the strip is placed so as to be nearly in contact with the glass. When the strip is in the middle of the containing vessel no movements are apparent.

The excess of pressure above the normal gas pressure that a heated surface experiences has been termed the thermo-kinetic reaction.

In the Crookes Radiometer the motion of the vane is caused by the difference of the thermo-kinetic reactions, due to the difference of the temperatures of the two sides of the vane.

In the Radiometer described above the initial motion of the strip is caused by the difference of the thermo-kinetic

* "Phil. Trans.," II, 1879, p. 768.

† "Phil. Trans.," I, 1879, p. 133.

reactions on the two sides of the strip, arising from their different distances from the walls of the containing vessel.

Under certain conditions, more complicated movements of the strip may occur. As it is proposed, however, to deal more fully with the subject in a subsequent Paper, further space will not be devoted to it here.

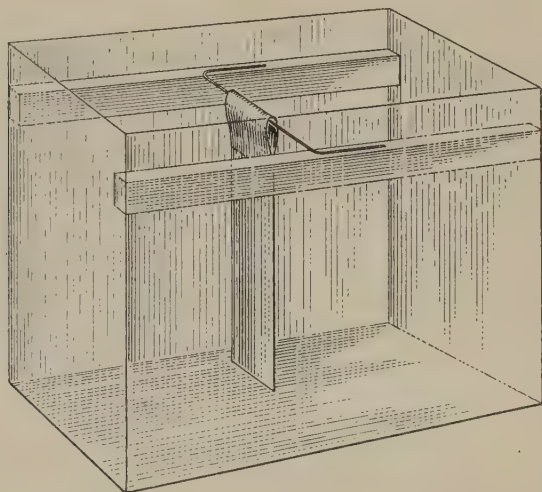


FIG. 5.

The Pressure of Radiation.

Under the new conditions, it is evident that to obtain trustworthy values of the pressure of radiation :—

- (i.) The strip should be as central as possible.
- (ii.) The vacuum should be very high.

The latter object was attained by the use of liquid air and charcoal. Further, only short exposures of about one second, were given, and the source of radiation was placed first on one side and then on the other. Any small deflection due to the difference of thermo-kinetic reaction on the two sides of the strip would therefore be eliminated by taking half the sum of the two readings.

The viscosity of a gas remains constant over wide ranges of pressure, but at very low pressures it is much reduced.* As a result, it was noticed that with liquid air vacua the strip was

* Crookes, "Phil. Trans.," 172, Part II., p. 378.

kept constantly vibrating like a pendulum by accidental tremors. The period of vibration was 0.45 sec., a value which agrees with the period of vibration of a flexible chain of the same length. A great advantage of the original apparatus, namely, its comparative insensitiveness to vibration, was thus lost at very low pressures. By mounting the apparatus, however, on the concrete floor of a basement, and by waiting for quiet intervals, some reasonably good results were obtained for the pressure of radiation. A series of results taken in succession is given below.

GOLD STRIP.

Liquid air vacuum. Energy density of radiation when lamp 10.5 cm. distant = 1.95×10^{-5} ergs /c.c. Length of strip = 7.10 cm. Length of folded part AC = 1.02 Mass of 1 sq. cm. of gold leaf = 1.82×10^{-4} gm.

Distance of source.	Deflections from lamp.			Deflections calculated from energy density.
	Lamp on left side.	Lamp on right side.	Mean.	
10.5 cm.	2.5×10^{-3} cm.	3.2×10^{-3} cm.	2.8×10^{-3} cm.	1.6×10^{-3} cm.
11.5 cm.	1.9	2.7	2.3	1.4
12.5 cm.	1.7	2.2	2.0	1.2

The reason why all the preceding results are too high has not been explained, and it is proposed to undertake further investigations on the matter. Other results obtained with the gold strip were also too high, but better results were obtained with the aluminium strip. They are recorded below.

ALUMINIUM STRIP.

Liquid air vacuum. Energy density of radiation when lamp is 10.5 cm. distant = 1.95×10^{-5} ergs /c.c. Length of strip = 7.43 cm. Length of folded part AC = 0.83 cm. Mass of 1 sq. cm. of aluminium foil = 1.16×10^{-4} gm.

Distance of source.	Deflections from lamp.			Deflections calculated from energy density.
	Lamp on left side.	Lamp on right side.	Mean.	
10.5 cm.	2.4×10^{-3} cm.	2.5×10^{-3} cm.	2.5×10^{-3} cm.	2.6×10^{-3} cm.
11.5 cm.	2.0	2.1	2.0	2.3
12.5 cm.	1.6	1.3	1.5	2.0

Other results obtained with the aluminium strip were similar to those above.

By inclining the tube it was found possible to increase the difference of the thermo-kinetic reactions on the two sides of the strip, but this effect was always comparatively small.

The results are similar to those obtained in the previous research. Moreover the disturbing effects which were then attributed to convection, were really effects of the same kind as those described in this Paper.

Starting at atmospheric pressure, the thermo-kinetic reaction increases as the pressure is diminished, until a maximum is reached at a pressure of about 0.002 cm. of mercury. Experiments on the pressure of light may be advantageously carried out as far below the maximum as possible, or as far above the maximum as convection currents will permit. The latter alternative is the easier, and appears to give more consistent results.

In conclusion, I have pleasure in thanking Prof. Lees for valuable suggestions, and for affording me every facility for prosecuting this research.

ABSTRACT.

The pressure of the radiation emitted by a carbon filament lamp at a distance of a few centimetres, is sufficient to cause a microscopically measurable deflection of the end of a strip of gold or aluminium foil, suspended in a closed test tube. By this means the radiation pressure may be measured, and the results may be checked by a comparison with the energy density of the radiation, as deduced from the initial rate of rise of temperature of an exposed blackened copper plate.

In a previous Paper, experiments were carried out in atmospheres of air and hydrogen, and at pressures extending from 76 cm. to 1 cm. of mercury. Under certain conditions it was found possible to obtain satisfactory results. The present Paper deals with experiments at pressures from 1 cm. of mercury down to the highest exhaustions that could be reached.

As the pressure is lowered, certain gas-action effects make their appearance, but, inasmuch as there is no appreciable difference of temperature on the two sides of the strip, the effects are somewhat different from those that occur in the ordinary type of Crookes' radiometer.

When the surface of the strip is closer to one side of the containing vessel than to the opposite side, a deflection away from the closer side occurs, and the direction of this deflection is independent of the side of the strip on which the radiation falls. With a symmetrically-placed strip the deflection should be negligibly small. An explanation of these effects is suggested in the Paper, and a special type of radiometer is described.

The nature of the residual gas in the tube does not seem to be very important, but it is found that the repulsive force acting on the strip increases with decreasing pressure, until a maximum is reached at about 0.002 cm. of mercury. With further reduction of pressure a progressive decrease takes place.

By symmetrical suspension, and by the use of liquid air and charcoal, it is possible so to reduce the gas action effect that measurements of the pressure of light of reasonable accuracy are again possible.

Experiments on the pressure of light may thus be advantageously carried out at the highest vacua obtainable, or at pressures as far above 0.002 cm. of mercury as convection currents will permit. The latter alternative is the easier, and leads to more consistent results.

DISCUSSION.

Mr. D. OWEN (communicated remarks) thought the author was to be congratulated on his determined attempt to eliminate gas action at the lowest possible vacua. It appeared, from the tables at the end of the Paper, that even at the lowest pressures the deflection of the leaf differed according to the direction of the incident light. Such dissymmetry as is thus implied in the apparatus might also account for the different effects obtained with gold and aluminium. Observations with much larger vessels appeared to be desirable. The optical arrangements might perhaps be modified to avoid the contiguity of the leaf to the microscope objective. Such conditions might also be expected to enhance the undoubted advantage of the author's method, namely, rapid attainment of the final state; in some of Poynting & Barlow's experiments as much as an hour was found necessary. Had the author found it practicable to calculate the gas pressures, at the highest exhaustions, from the damping of the foil?

The AUTHOR, in reply, stated that he was in agreement with Mr. Owen as to the desirability of using larger containing vessels. It was felt, however, that before attempting more accurate measurements, a fuller investigation of the gas action was necessary. Owing to the disturbing effect of incessant tremors it had not yet been found possible to obtain an estimate of the pressures at the highest exhaustions, by observing the degree of damping. A modification of the method of mounting the strips might make such observations possible.

XXVII. *The Viscosity of Suspensions of Rigid Particles at Different Rates of Shear.* By EDITH HUMPHREY, B.Sc., Ph.D., and EMIL HATSCHEK.

RECEIVED MAY 12, 1916.

THE present investigation was undertaken with the object of discovering the relation between the concentration, the rate of shear and the viscosity of a suspension of rigid particles in a liquid. As students of the colloid state know, the viscosity of colloidal solutions gives one of the criteria by which such solutions are divided into two classes: One class (*e.g.*, colloidal solutions of metals or metallic sulphides) shows viscosities very little in excess of that of the solvents; the other (*e.g.*, colloidal solutions of hydroxides, proteins, &c.) exhibits marked increase in viscosity. Rubber and nitrocellulose are extreme cases of this latter class, as solutions of less than 1 per cent. have viscosities 20 to 100 times that of the solvent. It has been generally accepted that these differences of behaviour may be explained as due to a difference in the form of the particles, or, as it is called, of the disperse phase. A suspension of solid, or, more properly, rigid, particles gives a low increase of viscosity, and the corresponding colloids are known as suspensoids; on the other hand, the great increase in viscosity is accounted for by the presence of liquid (or deformable) particles in emulsions or emulsoid sols.

The mathematical treatment of a suspension of rigid particles in a liquid must, of course, be confined to spheres of such size as to follow Stokes' law, but within these limits is quite simple.* Only the principle of the treatment need be given here: A layer of liquid containing in suspension small rigid spheres is being sheared between two parallel plates, one of which is stationary, while the other travels in its own plane. It is obvious that the transverse velocity of the liquid at the upper pole of any sphere will be greater than that at the lower pole, so that the spheres may be considered to have a translatory motion relative to the liquid, the velocity of which is equal to half the difference of the velocities at the two poles. The extra work done in moving the particles can be calculated on Stokes' formula, assuming that the particles do not interfere with one another—that is to say, that there is no turbulence.

* E. Hatschek, "Kolloid-Zeitschrift," VII., 301 (1910).

This work on the particles is done in addition to that expended in shearing the liquid, and may be added to it, the sum being the work required to shear the whole suspension, and thus the viscosity may be reduced, and is found to be

$$\eta_c = \eta_0(1 + 4.5f),$$

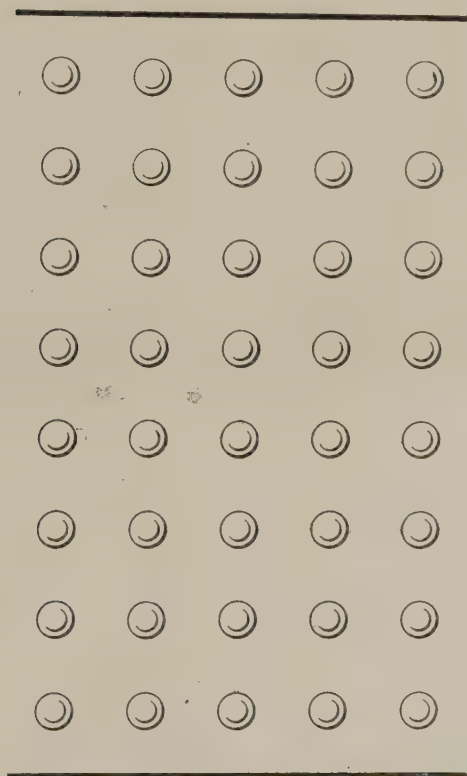


FIG. 1.

when

η_c = viscosity coefficient of the suspension of concentration C .

η_0 = viscosity coefficient of the liquid.

f = the ratio $\frac{\text{aggregate volume of solid particles}}{\text{total volume of suspension}}$.

Since the radius of the particles does not appear in the formula

the viscosity should be independent of the latter (a result which is somewhat surprising), and the increase in viscosity caused by the suspended particles should be simply proportional to the aggregate volume.

A similar result had been obtained by Einstein in 1906.* He deduced the viscosity of a suspension of spherical particles by thermodynamical methods, in a Paper on the determination of the molecular radius, and found the value

$$\eta_c = \eta_0(1+f),$$

which is identical with the formula given on previous page, except for the numerical constant.

This result had been entirely overlooked by colloidal chemists; although the viscosity of suspensions is discussed both in Freundlich's "Kapillarchemie" and in Ostwald's "Grundriss," no reference is made to Einstein's result in these standard works, both of which appeared in 1909. The formula was, however, noticed in 1910 by Bancelin,† who proceeded to test it experimentally on suspensions of gamboge made by Perrin's method, and consisting of particles of uniform size. He found that the linear law held good up to 3 per cent., irrespective of size, but that the proportionality factor was 2.9 instead of 1.

Bancelin drew the attention of Einstein to the divergence in the numerical constants, and Einstein revised his formula and found a new constant, 2.5. The method by which the revised result was obtained has never been published.

A set of determinations of the viscosity of suspensions of starches of different origin (and therefore of different size) was made by Harrison‡ in 1911. He found that the increase in viscosity was independent of the size of the particles and in linear ratio to the volume as found by centrifuging the suspension and reading the total volume occupied by the granules.

On the other hand, Sven Oden§ used a sulphur sol and found that the viscosity of more concentrated solutions increases more rapidly than the concentration, and also that the more disperse the sol (the smaller the particles) the greater the viscosity.

It seemed possible that some of these discrepancies were caused by the use of the capillary viscosimeter, and the present

* A. Einstein, "Ann. d. Physik," XIX., 289 (1906).

† M. Bancelin, "Koll.-Zeitschr.," IX., 154 (1911).

‡ Wm. Harrison, "Journ." Soc. Dyers and Colourists, XXVII. (April, 1911).

§ Sven Oden, "Zeitschr. Phys. Chemie," LXXX., 709 (1912).

investigation was undertaken with Hatschek's modification of Couette's apparatus, which allows of a variation of the rate of shear. This apparatus (Fig. 2) consists of a hollow cylinder A, which is supported by a wire, B, from a heavy bracket, C. The cylinder A is open and bevelled at the end, and is coaxial with an outer cylinder, D. Two short guard cylinders E and E' nearly closed at one end are placed opposite the open ends of cylinder A, leaving a clearance of about 2 mm. between the bevelled surfaces. The outer cylinder D rests on a table, F, which can be rotated. When the whole is filled with liquid and the outer cylinder is set in motion, a layer 0.5 cm. wide is sheared between the moving and the suspended cylinders. The consequent twist of the suspended cylinder is read by means of a mirror, G, attached rigidly to it above the level of the outer cylinder.

With the apparatus, as described so far, the viscosity of water, which from previous experiments is known to be constant within the limits of shear employed, showed a marked increase with rising rates of shear. It appeared that the effect of the revolving bottom of the outer cylinder was not entirely eliminated by the guard "E," but this was finally accomplished by fixing to the latter a thin plate, H, coming to within 1 mm. of the wall of the revolving cylinder. This reduced the increase in viscosity coefficient to 1 per cent. in the case of water and to 2 per cent. in the case of glycerine and water, when the angular velocity, and consequently the rate of shear, was increased between five and six times. Since the inside diameter of the outer cylinder is 11 cm. and the outside diameter of the suspended cylinder 10 cm., each degree of arc in the revolving cylinder is equivalent to 0.0959 cm., and its linear velocity is obviously half the actual rate of shear of the liquid layer per centimetre of depth.

As regards the choice of a suitable suspension, the field is not as large as would appear at first sight. The number of solids obtainable in microscopic particles of even roughly spherical shape is slight, and their specific gravities are mostly well over two.

The suspension finally chosen for experiment was that of rice starch in a mixture of carbon tetrachloride and toluene. Both liquids were bought as pure, and were only prepared by being dried over calcium chloride. The amounts of the two liquids were so adjusted that the starch granules remained suspended for several hours. The specific gravity in the

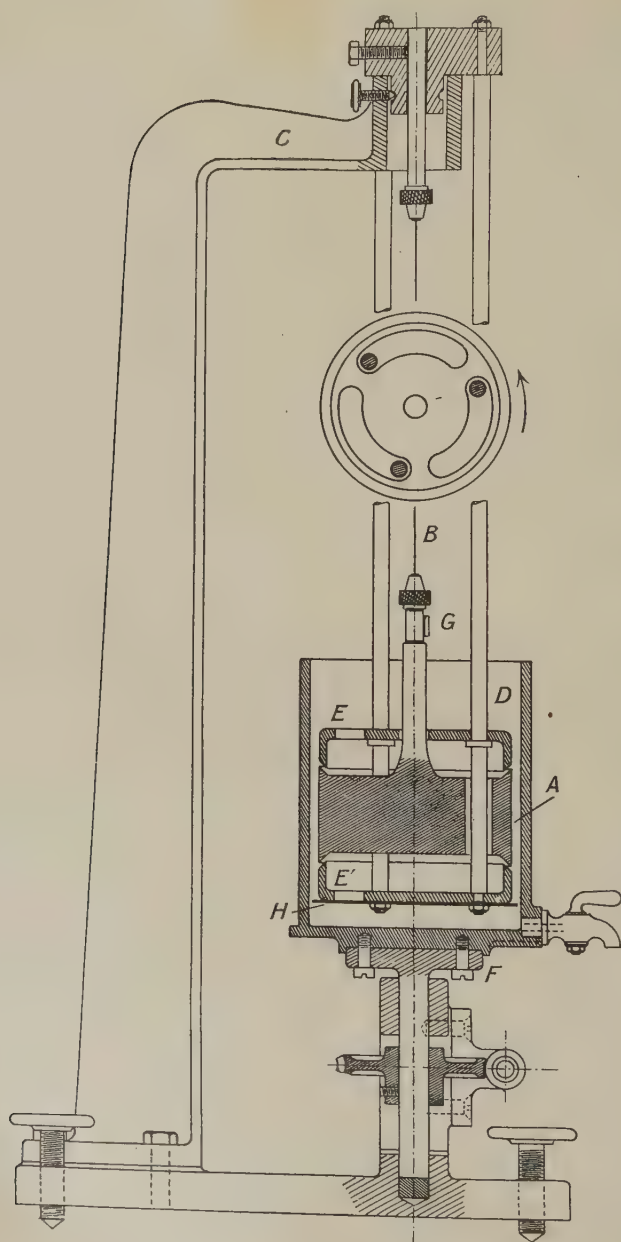


FIG. 2.

final set of determinations was 1.505 at 13°C. The starch used was pure rice starch, the granules of which are not spherical, but polyhedral, often hexagonal in section. By

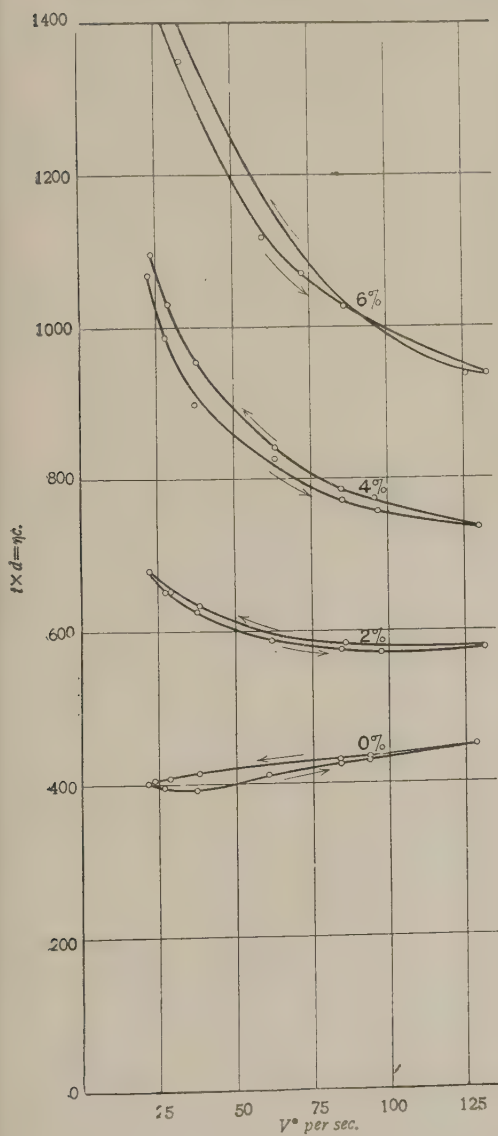


FIG. 3.

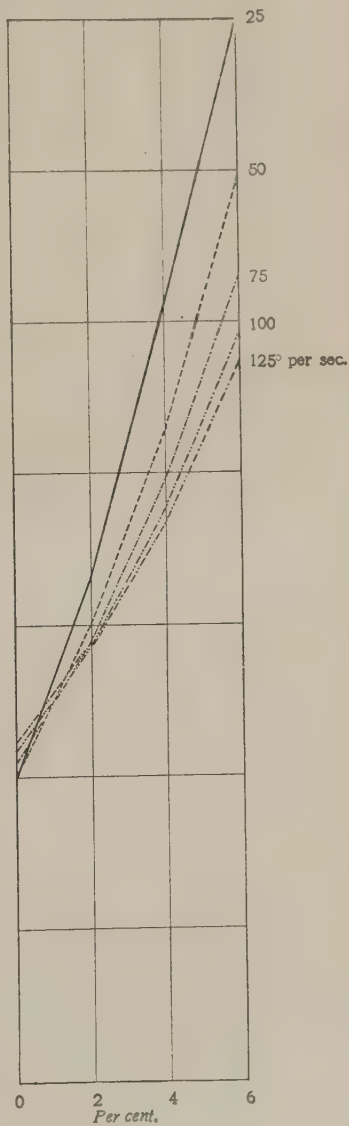


FIG. 4.

constant drying and sieving the larger granules were eliminated and those used finally were about 0.003 mm. in diameter. This starch was prepared by drying it at 100°C.; finally it was sifted and preserved in stoppered bottles, but it evidently took up a certain amount of moisture from the air. Preliminary experiments having shown no difference between old and new suspensions, the ordinary procedure was to make up a litre of the mixture some six to eight hours before the time of the determinations. The mixture was brought if necessary to the required temperature, and put into the viscosimeter. The zero was read and the cylinder rotated at its lowest speed; after a short run to obtain equilibrium, the time of a convenient number of revolutions was taken, and the position of the inner cylinder was read by means of the mirror. After a couple of concordant readings had been obtained the rotation was stopped until the cylinder had come to rest, when these operations were repeated at the next highest speed. After seven speeds had been used the process was reversed until the lowest speed was reached. The whole experiment occupied some two hours. At higher concentrations it was found better to tap the apparatus gently to get the true zero.

The systems treated were the 0, 2, 4 and 6 per cent. suspensions by volume, and the angular velocities varied roughly from 20 deg. to 180 deg. per second, corresponding to linear velocities of the revolving cylinder or 1.9 to 17.2 cm. per second.

Figs. 3, 4 and 5 show the results obtained. In Fig. 3 the products $d \times t$ are plotted against the angular velocities, the curves showing the behaviour for each concentration, while in Fig. 4 these same products are plotted against the concentrations, the curves in this case showing the behaviour of the various suspensions at the same speed. The model combines both of these, and completely defines the viscosity; all possible values of the viscosity (within the limits of the investigation) lie on its surface, the viscosity being a function both of the concentration and the rate of shear. The most noticeable result of the whole set of determinations is the marked dependence of the viscosity on the rate of shear. It is much greater at lower rates, but tends to approach constancy at rates above a certain limit, which limit itself increases with the concentration of the suspension.

This is clearly shown in Fig. 5, which gives the relative viscosities, *i.e.*, the ratio

$$\eta_c/\eta_0 \text{ at same rate of shear}$$

for a number of different velocities. If we use this curve to test the formula

$$\eta_c/\eta_0 = 1 + a \times \frac{\text{volume of disperse phase}}{\text{total volume}},$$

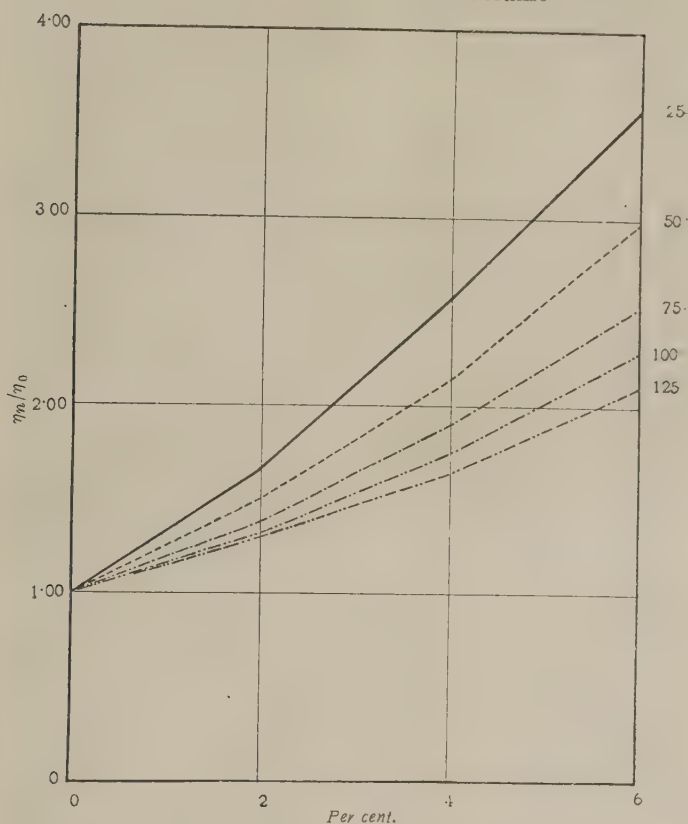


FIG. 5.

we obtain the following values :—

Concentration.	η_c/η_0	a
2 per cent.	1.3	15
4 per cent.	1.6	15
6 per cent.	2.1	18

Which show that at 6 per cent. the increase is more than linear at 125 deg. per second. Moreover, we see by the curves that the 2 per cent. suspension becomes irregular below 75 deg. (7.18 cm.) per second.

The deviations from the formula are, therefore, of two kinds, the increase in relative viscosity is more than linear, especially at low rates of shear, and the proportionality factor is much greater than the figure found theoretically. As regards the latter, the difference between spherical and irregular polyhedral particles may be sufficient to account for the discrepancy.

The more than linear increase probably points to this that the assumption on which both Einstein's and Hatschek's deductions are based—viz., that the particles do not influence one another—is untenable. In a 2 per cent. suspension of such particles as we have considered, the distance between adjoining particles, assuming them to be placed at the corners of cubes, would be less than four diameters from centre to centre or less than three diameters from surface to surface. With smaller particles, which would be correspondingly more numerous for the same aggregate volume, the distances would be considerably smaller still. It, therefore, seems quite possible that each particle will be impeded by the surrounding ones, a condition of things which hardly lends itself to mathematical treatment. If such interference between adjoining particles does take place, it is, however, obvious that both their absolute size and distance—in other words, the degree of dispersity and the concentration—must affect the viscosity of the system.

A possible source of error in the experiments described deserves mention. The starch used still contained imbibed water, and it is, therefore, possible that it was not completely wetted by the medium, a condition which would perhaps cause further and unknown complications. One experiment made with highly dried starch showed a viscosity much lower than could be explained by the decrease in volume due to the withdrawal of a few per cent. of water. We have settled on a suspension free from this defect, and hope to investigate it fully when conditions are more favourable.

We gladly take this opportunity for expressing our thanks to Dr. R. S. Willows for much valuable advice and assistance.

Physical Laboratory of the Sir John Cass Technical Institute.

ABSTRACT.

This investigation was undertaken with a view to testing the Einstein-Hatschek formula at variable rates of shear. According to this formula the viscosity of a suspension of rigid spherical particles grows in linear ratio with the aggregate volume of suspended particles,

and is independent of their size, as long as the latter conforms to Stokes's formula.

The suspension chosen was one of rice starch of 0.003 mm., and less, diameter, in a mixture of carbon tetrachloride and toluene having the same specific gravity. The measurements were carried out in a modification of Couette's apparatus, in which the deflection of a cylinder, suspended coaxially in another cylinder filled with the liquid and rotated at different speeds, is measured. All measurements were carried out at speeds below that at which turbulence sets in, so that the deflection was proportional to the product of viscosity \times angular velocity.

The results of the investigation are: (1) The viscosity of a suspension is a function of the rate of shear, and increases as the latter decreases, the difference being more marked at higher concentrations; (2) for all rates of shear the viscosity of the suspension increases more rapidly than the aggregate volume of suspended matter; (3) for any one rate of shear the relative viscosity of a suspension, *i.e.*, its absolute viscosity divided by the absolute viscosity of the medium at the same rate of shear, also increases more rapidly than the percentage of suspended matter, the divergence from the linear increase demanded by the formula becoming less as the rate of shear becomes greater, so that a linear law may possibly hold good at rates of shear higher than those attainable in the present apparatus without turbulence.

The general conclusion is that the assumption on which the Einstein-Hatschek formula is based, *viz.*, non-interference between adjoining particles, is not tenable in the case of suspensions containing between 2 and 6 per cent. of suspended matter.

XXVIII.—*Experiments with Mercury Jet Interrupters.* By
CAPT. C. E. S. PHILLIPS, *F.R.S.E.*

RECEIVED JUNE 28, 1916.

THE following experiments have been undertaken with a view to ascertaining what is the form of the mercury column issuing from a hole in the side of a rotating drum that is continuously supplied with mercury by centrifugal action.

Incidentally, some improvements in the general design of interrupters have suggested themselves.

The wide use now made of this method of regularly "making" and "breaking" the current in the primary circuit of induction coils points to the need for some such investigation as I have attempted, in order to increase, if possible, the efficiency of this important part of an X-ray equipment.

It was necessary, of course, that observations should be made within the interrupter itself while in action, and the following apparatus was therefore constructed. (Fig. 1.)

The working parts of the arrangement are contained in a cast-iron vessel, V, which stands firmly upon the wooden frame F, and measures 6 in. high and 7 in. in diameter.

It is closed at the top with an easily removable lid, which is fastened down upon a rubber washer by means of thumb screws.

The glass window G enables the drum D and the segments S S' to be seen while the interrupter is at work.

The revolving drum is attached to a spindle which passes down through the steel bush B and makes mechanical connection with the motor M, as shown in the figure.

The lower part of the drum dips into mercury held in the well W, and a small hole drilled in its base close to the spindle allows the liquid to enter.

The drum itself is made of vulcanite, for reasons to be given later, and so requires, on account of its buoyancy, to be held down under the mercury by the spring connection to the motor shaft. No foot bearing is therefore necessary, nor can gas escape through the sleeve, on account of the mercury seal.

The walls of the drum are parallel on the outside, but thicker at the base than at the top, and two holes, H H', 1.5 mm. in diameter, are drilled opposite to each other in the vulcanite to allow the mercury to escape when driven upwards by centrifugal force.

A rim at the top serves to prevent loss of mercury by spilling at excessive speeds, and assists in maintaining a good supply of mercury at the orifices $H H'$.

The metal segments $S S'$ are arranged symmetrically, as shown. They are capable of adjustment as to width, and are

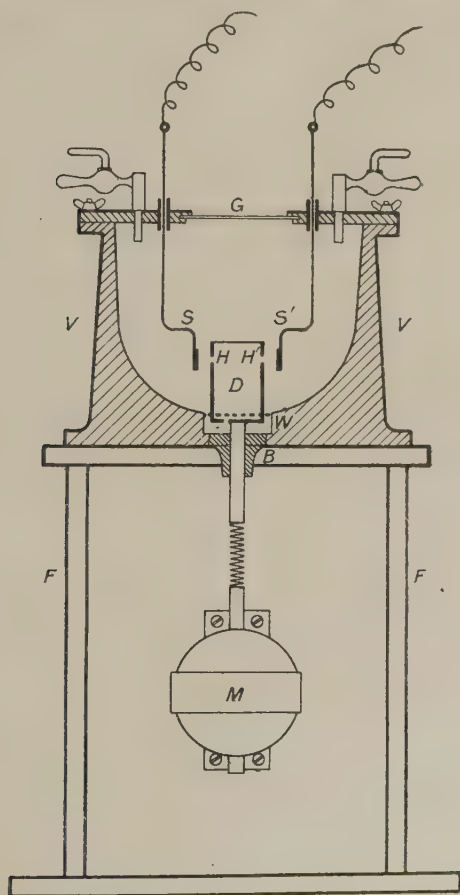


FIG. 1.

connected in series with the circuit which it is required to interrupt.

Taps are provided for the introduction of gas, and a small disc shutter is arranged to close the window in the lid when necessary. This apparatus is convenient for comparing the

effect of varying the size and form of the orifice through which the mercury issues, for observing the advantage, or otherwise, of changing the distance of the segments from the drum, or altering their shape, angle, or the material of which they are made. It is also useful for testing the efficiency of various volatile liquids introduced for the purpose of cutting down the flare due to the self-induction of the circuits usually dealt with.

The Form of the Mercury Column.

When the interrupter is in action it is seen that two bright arcs occur at each segment, one at the point where the mercury first impinges, and the other where the mercury column leaves the sharp edge. When a current exceeding 2 amperes is passed by the apparatus while connected to an induction coil, the second arc is markedly greater than the first, owing to the self-induction of the circuit, and if the current is still further increased a flare begins to develop where the mercury leaves the segment.

The arcs at "make" always occur with great regularity, but the current passed by the apparatus often becomes fluctuating as soon as flaring takes place at the moment of "break."

The two mercury columns are illuminated by both the arcs at "make" and the flares at "break," and since, for small currents, these always occur when the orifices are exactly in the same position relatively to the segments, the mercury columns may be easily observed, and appear to be stationary no matter how rapidly the drum is revolving.

In this way it is noticed that the mercury seems to pour out of the side of the drum in a continuous stream, and that its path is bent backwards.

A little consideration, however, will show that this is not a correct interpretation of the phenomenon.

For if the direction of rotation of the drum is clockwise, as shown in Fig. 2, we may imagine, for the sake of simplicity, that the mercury escapes from the hole H at regular intervals; that is to say, when the orifice has moved into the positions marked A, B, C, D, E, F respectively. At the moment when the mercury escapes from the orifice at A it is moving in a circular path with the velocity of the drum itself, so that if at the instant the mercury is free the radial component is nil (and in the case considered it is very small), the mercury, on

appearing through the orifice, will move off along a line, AO , which is a tangent to its original path. By the time that the orifice has reached the position F the mercury, if we disregard air resistance, will have reached the point 5 along AO , the length of $A5$ being equal to the circular arc AF .

Similarly, the mercury emitted when the orifice is at B will at the same instant have reached the point 4 along the line BO' , and the portion coming from the orifice when it is at C will reach the point 3 along the line AO'' , and so on.

If, now, these points are joined together, a curve is obtained which is seen to resemble closely that observed through the window of the interrupter when the mercury column is ren-

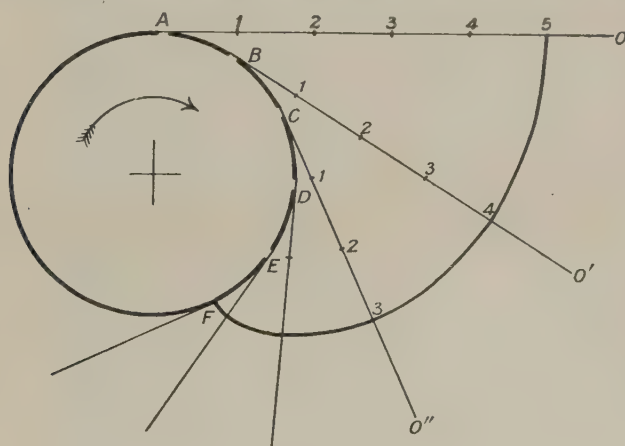


FIG. 2.

dered visible by the intermittent illumination occurring at the segments. But in actual practice the mercury flows out constantly through the orifices in the drum, with the result that continuous columns are produced which sweep round and serve the purpose of "making" and "breaking" the circuit. It must be borne in mind, however, that these columns are to be regarded as consisting of an infinite number of elements of mercury moving out from the drum tangentially, and therefore in directions normal to the concave aspect of the resulting curves. Under ideal conditions the columns would take the form of an involute of the circle represented by the drum's circumference.

Fig. 3 is a photograph of one of the columns taken by the light of the small arc that occurs at "make."

In cases where the drum is provided with radial jets the form of the curve becomes slightly modified.

Fig. 4 represents the breaking up of the column into globules which, in separating from one another, interrupt the current with great suddenness at the point where the mercury leaves the segment. High surface tension is of importance here, and it is, therefore, essential to keep the mercury not only apparently clean, but actually as pure as possible.

This is also advisable on account of the fact that a very small amount of contamination due, for instance, to the presence of a trace of soluble metal, strongly increases the tendency of the mercury to oxidise.

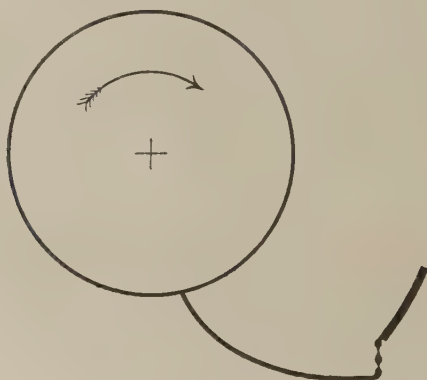


FIG. 4.

I have, therefore, tried to find a metal which would be more suitable for the segments than the copper in common use, and, so far, the most successful results have been obtained with tantalum.

This substance is not "wetted" by the mercury, it remains bright and clean indefinitely; it is easily worked and its high melting point renders it very durable.

Its one objection at the present time is comparative rarity and high cost.

The interrupter which is shown at work to the Society is fitted with tantalum segments, and it will be seen that the last 3 mm. at the edge where the mercury leaves are turned abruptly towards the drum to ensure greater regularity of action.



FIG. 3.

To face p. 288.

Experiments upon the best distance at which the segments should be placed show that the resistance of the mercury column is very appreciable, and that the interval between that portion of the segment where the break occurs should not be more than $\frac{3}{16}$ in. from the drum.

By placing the segments so that their curvature conforms to that of the mercury column itself the "make" current would be diminished somewhat owing to the greater length of the mercury initially intercepted by the segment. In X-ray work it seems desirable to check the rate of growth of the current in the circuit and this point may, therefore, be of some practical use.

Experiments with differently shaped orifices in the drum vertical slits, horizontal slits, &c., of various sizes have given no better results than can be obtained with the usual hole of about 2 mm. in diameter. It does not seem to matter, in fact, how much larger the hole is than this, for the mercury column appears to be approximately of the same thickness in spite of increased diameter of the orifice; nor with a long vertical and narrow slit can a ribbon of mercury be obtained. In extreme cases several small columns may appear, but never a ribbon. Consideration of Fig. 2 and the explanation given of it will show that this result is to be expected. Thicker columns can, however, be obtained by enlarging the holes in the drum, and covering them with short tangential tubes closed at one end and drawn down somewhat at the other, but with a large opening in their sides in register with those in the drum. If a good supply of mercury can be delivered to such tubes they can be arranged to emit a stream of any required diameter.

One common fault of modern mercury interrupters is the poor insulation of the jets in the region of the orifice. It is customary to use radial arms of metal connecting with the mercury in the well, and requiring insulating shields round the orifices to prevent irregular contacts due to back-splash. In the interrupter which I have described this is avoided by employing as rotating drum a vulcanite cylinder so that the back-splash from the segments, provided it is not allowed to interfere with the continuity of the column itself, a simple matter, is entirely prevented from producing irregularities.

Finally, some experiments have been carried out with a view to finding a substitute for coal gas (which is not always available) in reducing the flare that occurs at the moment of "break."

Of all the volatile liquids tried, ether was found to be by far the most effective.

The exceptional behaviour of coal gas, hydrogen or ether is a matter of interest, and the usual explanation depending upon the high specific heat of hydrogen certainly cannot apply in the case of ether. It may be that the action has to do with changes of a totally different nature occurring in either substance, or that their effectiveness depends upon a possibly increased surface tension of the mercury in their presence.

An attempt to work the interrupters under compressed air has not proved a success up to a pressure of five atmospheres.

If it is desired to employ a very heavy current, recourse must be had to multiple jets, and by that means as much as 40 amperes at 200 volts can be safely passed by interrupters suitably designed for the purpose.

In conclusion, I wish to express my thanks to Mr. F. Rowe, who has kindly assisted at these experiments, and who has himself made most of the necessary apparatus.

ABSTRACT.

The Paper describes an experimental attempt to ascertain the form of the mercury column issuing from a hole in the side of a rotating drum, that is continuously supplied with mercury by centrifugal action.

Incidentally a new form of interrupter is introduced, in which the interior is visible through a window in the lid. The arrangement forms a suitable apparatus for experiments with various forms of orifices and metallic contact segments, and the Paper gives an account of work in that direction. As it is important to ensure the cleanliness of the mercury in interrupters of this type, the usual copper segments are replaced by ones made of tantalum, which, for many reasons is preferable. It is not "wetted" by mercury, it remains clean and bright indefinitely, and its high melting point renders it lasting.

Experiments with various forms of orifice are described, and it is pointed out that the issuing stream is only slightly affected by this means. An explanation is given of the fact that a vertical slit orifice will not produce a ribbon of mercury, and that no matter how much the diameter of the orifice is increased beyond about 2 mm., the cross section of the mercury column remains unaltered. A method is described, however, by which a much larger stream of mercury can be obtained from the rotating drum, if necessary.

Brief reference is made to experiments with various volatile liquids in suppressing the flare which occurs when the mercury columns leave the contact segments. The three well-known substances which are most effective in this respect are coal gas, hydrogen and ether.

It is pointed out that experiments of this nature are necessary, in view of the wide use now made of mercury interrupters in X-ray work.

DISCUSSION.

Capt. REID thought the instrument described by the author was of considerable importance. In practice it would be a great advantage to see the interior of the instrument when anything went wrong.

Dr. R. S. WILLOWS congratulated Capt. Phillips on having broken new ground in his experiments. Mercury interrupters had not been very scientifically investigated so far. He thought experiments on the thickness and resistance of the jet, on the resistance at the contact with the tantalum vane, and on the effect of varying the inductance of the primary circuit on the performance of the interrupter, would yield results of importance. Had the best shape and inclination of the plate on which the jet impinged been worked out? With regard to the effect of different gases in quenching the flare, he thought the specific inductive capacities were the determining factor rather than the specific heats. The same problem was met with in running a singing arc.

Mr. G. L. ADDENBROOKE mentioned that one firm he knew of made interrupters with an electrode of variable inclination.

Mr. P. R. COURSEY (communicated remarks): The author has touched upon one of the main difficulties encountered in practical work with the modern forms of mercury break, viz., that it is usually quite impossible to inspect the operation of the break while it is in use, or to see at once what is wrong if it does not work satisfactorily, without in many cases completely dismantling the apparatus. In some experiments which I carried out some time ago upon the subject, a special form of break* was constructed both with this object in view and for the purpose of handling fairly heavy currents. The whole of the working parts are carried by an insulating top supported on a stout glass jar, and may therefore be easily lifted out bodily when required by releasing the clamping screws, while at the same time the operation of the break is always open to view. Various sized jets up to about 4 mm. diameter (the full bore of the pump holes) were employed in different experiments, but as is pointed out in the Paper, little advantage is shown by the large jets, as compared with the small ones, owing to the tendency of the jet to break up from a solid stream into separate globules, unless the gap between the jet hole and the fixed electrode is kept very small. When this is the case it becomes almost essential to keep the electrode surface concentric with the exterior of the pump, as otherwise small clearances cannot be maintained. The author's method of securing a solid jet is particularly interesting in this connection. Considerable improvement in the operation of mercury interrupters, and elimination of the sparking at the contacts, may usually be secured by electrically tuning the discharge circuit to approximately the same frequency as that of the interruptions by means of a condenser connected either directly across the interrupter terminals, or, preferably (especially with a supply of 100 volts or more) across both the interrupter and induction coil primary in series. A suitable choking inductance and resistance must be inserted in the supply leads with this arrangement. The value of the inductance in series with the interrupter is usually of considerable importance in securing maximum output, and most satisfactory and steady operation of the break with the minimum of internal sparking, and the value that is most suitable is best found by trial in each case, its action in conjunction with the condenser being to control the rate of rise and fall of the current, so that the circuit is broken in each case at the most favourable point on the current wave. These arrangements, by reducing the sparking, lengthen the time during which the interrupter can be used before cleaning of the mercury becomes necessary.

Capt. PHILLIPS, in reply, said that some of the points raised by Dr. Willows were dealt with more fully in the Paper than in his description.

* "Electrician," Vol. LXIX., p. 899, 1912.

The resistance of the jet was a very interesting point, and he had some experiments in progress on the matter. He was not quite clear whether the seat of the resistance was the mercury column or the junction of the column with the electrode. The position of the electrodes was also dealt with in the Paper.

In reply to Mr. Coursey : The interrupter devised by Mr. Coursey recalls that introduced some 20 years ago by Dr. Max Levy, which was also enclosed in a glass cylinder. Mr. Coursey does not say if his interrupter is required to work in an atmosphere of coal gas, but I presume that to be the case, and it is therefore open to the objection that if by accident an explosion occurs within, the whole apparatus is shattered. The window in the instrument exhibited may be made of non-flam celluloid, and is replaced in a few minutes if necessary. It is also desirable to be able to look down on the stream rather than to view it from the side. I am very interested in Mr. Coursey's references to the use of capacity and inductance in the interrupter circuit, and think that further experiments in this direction would be worth while.

XXIX. *A Sensitive Magnetometer.* By P. E. SHAW, B.A.,
D.Sc., and C. HAYES, B.Sc.

RECEIVED MAY 22, 1916.

IN a research recently published by one of us* there is a description of a torsion balance of special delicacy for gravitation research. A diagrammatic representation of this apparatus is

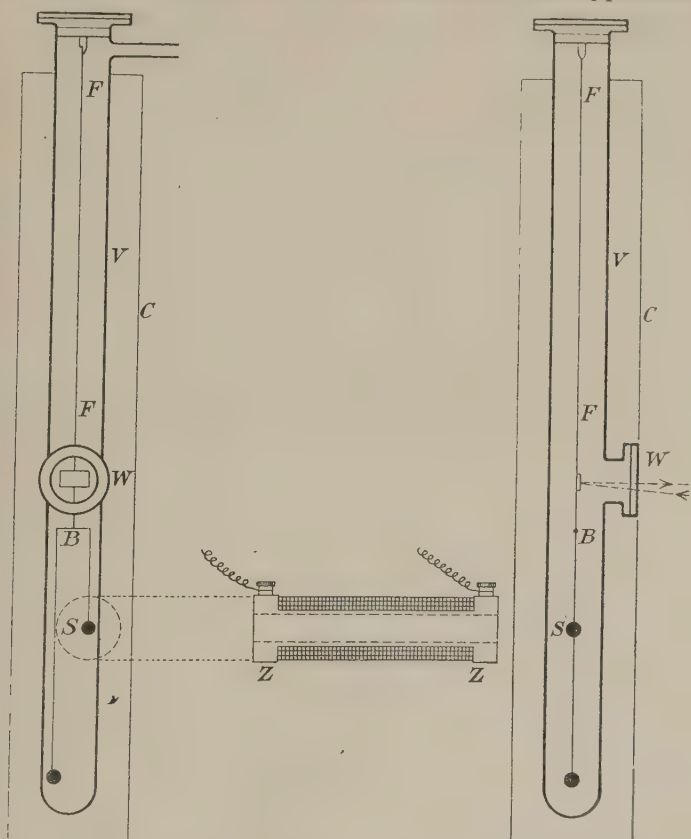


FIG. 1.—FRONT AND SIDE VIEWS OF THE MAGNETOMETER.

The axis of the solenoid is, as shown, in the first case perpendicular to the plane of the paper and in the second case in the plane of the paper.

shown in Fig. 1. A fibre, FF , 600 mm. long, 15μ diameter, carries a beam, B , 35 mm. long, from the ends of which are

* "The Newtonian Constant of Gravitation as Affected by Heat," Shaw, "Phil. Trans.," 1916, A. Vol. CCXVI., p. 349.

hung, by fine wires of length 150 mm. and 350 mm. respectively, two small spheres of silver, each weighing about 3 gm. This torsion system is hung in a low vacuum of about 15 mm. pressure. The movements of the torsion beam, carrying a mirror which reflects a distant scale, are observed through the window *W* by a powerful telescope distant about $4\frac{1}{2}$ metres. The vacuum tube *V* is wrapped by several layers of cotton-wool, and this latter is surrounded by a helix of lead "compo" tubing. The cylindrical envelope *C* encloses the cotton-wool and tubing, and all the vacuum tube except the extreme upper portion. The lead helix contains cold water. Further details of this apparatus are given in the Paper quoted.

In the course of the research mentioned it was necessary to heat the vacuum tube. This was attained by the passage of a current through a coil of wire wrapped on the outside of the vacuum tube. It was found later that on account of the field thus produced the silver spheres had become permanently but weakly magnetised with vertical axes. This permanent magnetisation was observed as follows: When the *N.* pole of a bar magnet, 20 cm. long, was brought to about 6 cm. from one sphere, the latter moved, and a scale deflection of several centimetres (right or left, according as the pole was above or below the sphere) was observed. The coercivity was considerable; the field required to remove the permanent magnetism from the spheres being of the same order as that used in its production. After much trial the required field was obtained, and the vertical permanent magnetism was so far removed that the scale deflection due to the presence of the *N.* pole, was reduced to less than 0.5 mm.

The spheres were of silver of the highest purity from Messrs. Johnson, Matthey & Co., who described it as "absolutely pure." Care was taken, during the mounting of the spheres on the torsion system, to avoid any contamination of their surfaces. Clean hands were used by the operator, and after mounting and before entering the vacuum tube, they were washed in nitric acid, followed by distilled water.

This behaviour of such pure silver came as a surprise. One did not expect either silver or the small amount of residual iron to display permanent magnetism and great retentivity. So an investigation was commenced to ascertain the nature of these effects.

Some scraps of the same silver as used for making the spheres were analysed. Specially pure nitric acid was tested, and

found by the ferrocyanide test to be free of iron. The silver scraps were then dissolved in this nitric acid. After boiling off any excess of acid, iron-free hydrochloric acid was added, and the silver chloride precipitated. The iron was left in the solution, which was now tested by the colorimetric ferrocyanide test. The result of the analysis was that the proportion of iron to silver was found to be 30/1,000,000. The silver spheres were probably much purer than the scraps used in the analysis, as the latter were the turnings from the spheres.

After searching for authorities on the subject of the susceptibility of the less magnetisable elements, the work of Honda* was taken to be the best on silver up to date. The method employed by Honda was to place a small quantity of the silver in a capsule carried by a torsion beam and to observe the couple produced on the beam when a very powerful field was applied by an electro-magnet near the capsule. He then deduced that the susceptibility of silver is $K = -2 \times 10^{-6}$ c.g.s.

In order to observe the effects of a field on our suspended silver spheres, we brought up a solenoid, ZZ, of length 38.5 cm., outside diameter 10.8 cm. and having 528 turns of about 16 S.W.G. copper wire, close to the vacuum tube, opposite to the upper sphere S, so that the axis of the solenoid was horizontal, and passed through the centre of the sphere. On passing currents through the solenoid and an ammeter, the field developed at the sphere was varied from 1.3 gauss to 12.0 gauss. The silver sphere being in a divergent field, was urged along the axis of the solenoid and a scale deflection was read by the telescope. As silver is diamagnetic we expected that the sphere would be repelled. But, on the contrary, there was an attraction to the solenoid. Thus, there must be, apparently, sufficient iron impurity present to give it a preponderating effect over the diamagnetic silver. For fields of about 5 gauss, iron has a susceptibility of about 170 c.g.s. Then, supposing silver and iron act independently in a magnetic field in the presence of one another, the proportion of iron to silver in our sphere must considerably exceed 1 to 80,000,000. But we have no authority for supposing that this principle of proportionality holds good. The experimental evidence is, in fact, that the iron loses some or all of its magnetic power when melted into other metals. To quote two examples of this principle:—

* "Ann. der Physik.," XXXII., pp. 1027-1063.

1. A certain alloy of iron and nickel can be made, which has practically no ferromagnetic qualities. Thus each of these strongly magnetic metals loses magnetism through the presence of the other.

2. Honda* found that for *very large fields* the magnetic influence of the iron impurity is never more than 50 per cent., and sometimes as little as 5 per cent. of that which it would be on the basis of proportionality.

After obtaining the above preliminary result, the current in the solenoid was varied from 2 to 9 amperes (Table I.) and the scale deflections noted. Next, the solenoid was moved along its axis nearer to the silver sphere, and the experiment repeated with the currents 1 to 9 amperes (Table II.). Details as to the form and use of the torsion balance will be found in the gravitation research, as quoted.

TABLE I.

Current. Amps.	Field H .	$\frac{\partial H}{\partial x}$	d_1 . mm.	d_2 . mm.	$K_a \times 10^6$.
2	1.81	0.40	2.24	0.49	0.176
3	2.72	0.46	4.83	2.45	0.272
4	3.63	0.60	8.43	4.53	0.277
5	4.53	0.80	12.33	8.20	0.264
6	5.44	0.98	17.37	12.00	0.258
7	6.35	1.14	23.35	17.17	0.262
8	7.25	1.30	28.50	21.45	0.248
9	8.16	1.42	35.23	28.78	0.258

TABLE II.

Current. Amps.	Field H .	$\frac{\partial H}{\partial x}$	d_1 . mm.	d_2 . mm.	$K_a \times 10^6$.
1	1.34	0.29	1.17	0.17	0.159
2	2.67	0.57	4.98	2.03	0.214
3	4.01	0.72	10.65	6.30	0.274
4	5.34	1.14	21.13	12.28	0.256
5	6.68	1.45	28.15	20.93	0.236
6	8.02	1.76	39.95	31.25	0.235
7	9.35	2.02	53.93	42.10	0.237
8	10.69	2.29	71.91	59.39	0.250
9	12.02	2.59	88.19	75.31	0.245

It should be observed that care was taken throughout to have the silver sphere in a cyclic state. Before commencing the readings in Table I. the largest field about to be used

* *Loc. cit.*

was developed in the solenoid, and this field was slowly reduced with alternations until it became zero. Again, before every reading, direct or reverse, the current in the solenoid was reversed, say, 10 times.

To Find a Value for the Susceptibility of the Silver Used,

Let

K = Susceptibility of absolutely pure silver.

K_a = Susceptibility of the (impure) silver used.

V = Volume of the sphere.

a = Arm of the torsion balance.

G = Couple required to produce a deflection of 1 mm. on the scale. (In this apparatus G has the small value 4.5×10^{-7} dyne cm.)

P = Permanent magnetism (this is a magnetic moment).

Then the sphere is in a divergent field whose gradient along the axis of the solenoid is $\partial H / \partial x$; and we have then—

For a Direct Current—

Couple acting on torsion balance

$$= (VK_a H + P) H / \partial x. a = G \cdot d_1, \dots \quad (1)$$

where d_1 = scale deflection.

For a Reverse Current—

$$\text{Couple} = (VK_a H - P) \partial H / \partial x. a = G \cdot d_2, \dots \quad (2)$$

where d_2 = scale deflection.

Whence—

$$K_a = \frac{G(d_1 + d_2)}{2VH\partial H/\partial x \cdot a} \dots \dots \dots (3)$$

The value of H is calculated from the usual expression—

$$H = 2\pi ni(\cos \beta - \cos \alpha),$$

and $\partial H / \partial x$ is calculated from a graph for H/x , specially drawn for the purpose.

The last column in Tables I. and II. show the values of K_a , ascertained from equation (3). Notice that the values of d_1 and d_2 differ considerably, showing that the permanent magnetism is an important factor.

The results for $H-K_a$ are shown in Fig. 2. It will be seen that the value of K_a rises with an increasing field, and attains a maximum for a field $H=3.0$ gauss. This is the field which gives the maximum susceptibility for pure soft iron, and we might expect that, since the value of K for iron drops rapidly as the field increases thereafter, the curves in Fig. 2 would also drop rapidly. But, in fact, the value of K_a is practically constant with increasing field. This means that, at least for fields of 3.0 to 9.0 gauss, either the values of K for iron and for silver vary together, or neither of them changes. Supposing (as is generally done) that the susceptibility of *pure* silver is constant, then that for the iron impurity is also constant over this range.

Honda worked with the range of field 5 to 23 kilo-gauss, and in the case of the slightly impure silver used, he found only a

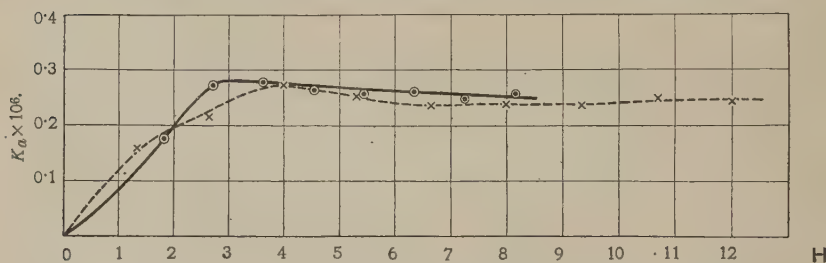


FIG. 2.—CURVE SHOWING THE RELATION OF FIELD IN GAUSSSES TO APPARENT SUSCEPTIBILITY $\times 10^6$.

small change in the susceptibility (at most about 30 per cent. of the whole) for this range. The proportion of iron to silver in his specimens was about 6/1,000,000 (as shown by chemical analysis). For these fields the effect was diamagnetic—*i.e.*, the silver effect preponderates over that of the iron. This again is another disproof of any simple superposition theory, as the figures for purity and susceptibility show.

For the very large fields used, Honda found a hyperbolic relation—

$$\chi = \chi_{\infty} + \sigma/H,$$

where

χ = Specific susceptibility for the silver specimen in a field H .

χ_{∞} = Specific susceptibility for an infinite field.

σ = A constant, the specific intensity of magnetisation for the iron impurity.

In our experiments there is no trace of a hyperbolic relation; in which case σ , in the above expression, is not constant, but variable.

Two researches other than that of Honda should be noticed:—

(1) A. P. Wills* worked on weakly magnetic bodies with fields of 1 kilo-gauss and upwards. He failed to establish any permanent magnetic state in the substances used. For these high fields the permanent magnetism would have been very small in proportion to the temporary magnetism, and in any case would be imperceptible, except with such a delicate instrument as was used by us.

(2) Fleming and Dewar† worked on silver at low temperatures for high fields only (2 to 3 kilo-gauss).

The above are the only recent researches at all kindred to ours which we have discovered.

It would have been interesting to extend the investigation by increasing the field and by varying the purity of the silver sphere, but as the torsion system was required for further research on gravitation (*see* introductory remarks), the vacuum could not be opened, and the investigation extended. We are thus forced to leave the problem at this stage, having satisfactorily tested the magnetic qualities of the spheres for low fields, which alone are important as regards the gravitation research.

We suggest that on a torsion balance of extreme delicacy such as that used by us (which is about 10^6 times as sensitive as that used by Honda), it would be possible to carry out a systematic investigation of the magnetism of feebly magnetic materials even for weak fields. This would be untrodden ground.

ABSTRACT.

A torsion balance of extreme delicacy carries a pair of purest silver balls, each 3 gm. weight. A solenoid with horizontal axis passing through one of the silver balls, is brought close to the balance. On exciting the solenoid, divergent fields of known strength are obtained in the region of the ball. The resulting attraction of the ball to the solenoid is shown by a mirror reflecting a distant scale to a telescope. The couple on the torsion beam required to produce 1 mm. scale deflection is 4.5×10^{-7} dyne cm., and this torsion balance is 10^6 times as sensitive as any known to have been used previously in this kind of work.

* "Phil. Mag.," May, 1898.

† "Proc." Roy. Soc., p. 311, 1898.

The results of these experiments are :—

1. The magnetic properties of the silver are ascertained even for weak fields of 1—10 gauss.
2. The silver has a pronounced retentivity; this effect being presumably due to the small trace of iron impurity.
3. The relation of susceptibility of the silver to the field used is found. The susceptibility of each of the constituent materials (*a*) pure silver, (*b*) residual pure iron, appears to be greatly modified by the presence of the other material.

DISCUSSION.

Dr. S. W. J. SMITH thought that the results obtained by the authors, showing the susceptibility of nearly pure silver in weak fields, were both interesting and instructive. He thought the authors, in discussing their significance, had overlooked the fact that the minute amount of iron (not exceeding 30 parts per million) shown to be present by chemical analysis, would not have the same effective susceptibility as iron in the form, for example, of long rods magnetised in the direction of their length. It was true that iron, when alloyed with other substances, could lose its characteristic ferromagnetic properties; but there was no reason to suppose that it would do so when present in silver, except in so far as the properties of a very minutely divided substance might differ from those of the same substance in bulk. So far as he knew, iron and silver were mutually insoluble. In that event the impurity found to be present should be regarded as minute particles of iron scattered about in a matrix of silver. To obtain an approximate idea of the effect of these particles upon the susceptibility of the material as a whole, it would be sufficient to regard them as spheres. Since the apparent susceptibility of a sphere is equal to $K/(1 + \frac{4}{3}\pi K)$, where K is the true susceptibility, and since the true susceptibility of iron in weak fields is considerable, the apparent susceptibility of such spheres would be practically constant in weak fields and equal to $3/4\pi \approx 0.24$. Hence, if the fraction of the total volume occupied by the iron were $n \times 10^{-6}$, the observed susceptibility of the material would be of the order $K_a = (0.24n - 2)10^{-6}$, where -2×10^{-6} represents the susceptibility of the silver. It was found by the authors that the susceptibility was practically constant over the range $H=4$ to $H=12$ c.g.s., and approximately equal to 0.25×10^{-6} . This would agree with $n \approx 9.4$. In other words, the results would indicate that the amount of iron present as impurity was of the order 10 parts per million (by volume). The curves given by the authors seemed to show that the apparent susceptibility varied considerably in fields lower than $H=4$; but part of the appearance of variability was due to the fact that, by inadvertence, the curves had been made to pass through $K_a=0$ at $H=0$. A possible source of uncertainty in the measurements in the weaker fields was the relatively great importance, under these circumstances, of P , the (assumed) permanent magnetism of the sphere. It seemed unlikely that the value of K for the iron in the weaker fields would be such as to make the effective susceptibility much less than $3/4\pi$, although there would be some tendency in this direction. The conclusion which he would draw from the data would be that the magnetic analysis of the material agreed with the chemical analysis and supported the inference, from other experiments, that iron and silver are mutually insoluble. The results obtained in strong fields (by Honda and others) did not, as the authors suggested, conflict with this conclusion, but confirmed it. The diamagnetic susceptibility of silver probably remains constant as the field strength is increased (within experimental limits); but, in intense fields, the susceptibility of iron is small compared with $3/4\pi$. For

instance, in fields of the order 25,000 c.g.s., the value of K may be of the order 0.1 to 0.05. Taking the latter figure, the effective susceptibility of the iron spheres would be approximately 0.04. The observed susceptibility of the material as a whole would be of the order $K_a = (0.04n - 2)10^{-6}$. Hence, assuming the value of n already deduced, we should expect K_a to be of the order -1.6×10^{-6} . Therefore, we should expect that the material used by the authors would become diamagnetic in strong fields. That it would, in fact, behave in such fields like the silver, of similar purity, examined by Honda.

Dr. CHREE said it was of the utmost importance in working with weak fields to get rid of effects due to electric tram and railway systems. This was not an easy matter nowadays. He had expected to hear some reference to the bearing of these results on Dr. Shaw's gravitational experiments, and would like to know if the magnetic experiments had caused any modification in Dr. Shaw's conclusions on the effect of temperature on gravity.

Prof. BOYS said that in his own experiments on gravitation, and also in the design of the radio-micrometer, the magnetism of impurities had always to be considered. The magnetic forces involved are so minute, that in most instruments—galvanometers, for example—they are ignored. In the radio-micrometer the field that could be employed was limited by the magnetism of the purest copper that could be obtained. He had drawn some copper himself which, after being cleaned with acid and gilt to protect it from air, had worked very satisfactorily. In the case of his gravitation experiments, he had used gold balls, of the greatest purity the Mint could supply, cleaned with nitric acid. No consistent magnetic disturbances were detected on moving a permanent magnet about in their neighbourhood.

Dr. SHAW, replying for the authors, was gratified that Dr. Smith's calculations had confirmed their numerical results. His theoretical treatment had been very instructive, and had enlightened them on several important points. He would like to ask Dr. Smith if superposition of magnetic properties would still occur in the case of two mutually soluble metals?

Dr. SMITH: In general, no.

Dr. SHAW, continuing, said, in reply to Dr. Chree, that in order to test whether the magnetic force between the large lead spheres and the silver spheres would vary appreciably with temperature in the gravitational experiments, he had inserted an iron bar in one of the lead spheres, but even then he had been unable to detect any variation in the force exerted on the silver when the lead and its contained rod were heated to 200°C. Since the magnetic material in the lead was very much less than this in the actual gravitation experiments, it was certain that the results were not affected by thermo-magnetic phenomena.

XXX. *The Latent Heat of Fusion of a Metal and the Quantum-Theory.*—II. By H. STANLEY ALLEN, M.A., D.Sc., University of London, King's College.

RECEIVED MAY 19, 1916.

§1. IN the first part of this Paper, read before the Society on May 12, 1916, I discussed the application of the quantum-theory to the calculation of the latent heat of fusion from the point of view of Einstein and also of Debye. The present communication contains a criticism of a theory of the process of fusion recently put forward by Ratnowsky.* Apart from the fact that the theory is based on a number of assumptions, several of which are open to serious objections, it will be shown that some of the results are rendered incorrect by an error in the mathematical analysis.

§2. *The Theory of Ratnowsky.*—The author of the theory considers the entropy of a substance in the solid, and also in the liquid state. He assumes that the whole internal energy, U_N , of the gram atom is made up of two parts, the vibrational energy E_N and the potential (volume) energy $f_N(v)$, so that

$$E_N = U_N - f_N(v).$$

By employing Boltzmann's equation, the entropy is determined by the formula†

$$S_N = \Sigma k \left\{ \left(1 + \frac{U - f(v)}{h\nu} \right) \log \left(1 + \frac{U - f(v)}{h\nu} \right) - \frac{U - f(v)}{h\nu} \log \frac{U - f(v)}{h\nu} \right\}.$$

The temperature T is given by the fundamental relation $\frac{\delta S}{\delta E} = \frac{1}{T}$, from which it follows that

$$U = \frac{h\nu}{e^{h\nu/kT} - 1} + f(v).$$

The entropy may then be obtained in the form

$$S_N = \Sigma k \left\{ \frac{\xi}{e^{\xi} - 1} - \log (1 - e^{-\xi}) \right\},$$

where $\xi = h\nu/kT$.

* Ratnowsky, "Deutsch. Physikal. Gesell. Verh.," Vol. XVI., p. 1033, 1914.

† In the first part of my Paper Boltzmann's constant, the gas constant for a single molecule, was represented by R . It is preferable to denote it by k , and to reserve R for the gas constant for one gram molecule.

The summation for various frequencies is carried out by assuming with Debye that the number of vibrations within a vibration interval dv is equal to $9Nv^2 dv/\nu_m^3$, where ν_m is the maximum vibration frequency, and N the number of atoms per gram atom. Then, putting $h\nu_m/kT=x$,

$$S_N = \frac{9Nk}{x^3} \int_0^x \left\{ \frac{\xi}{e^\xi - 1} - \log(1 - e^{-\xi}) \right\} \xi^2 d\xi.$$

Integration by parts reduces the expression to the form

$$S_N = \frac{3Nk}{x^3} \left\{ 4 \int_0^x \frac{\xi^3 d\xi}{e^\xi - 1} - x^3 \log(1 - e^{-x}) \right\}.$$

§3. Ratnowsky then proceeds to deduce an expression for the entropy for small values of x , of the form

$$S_N = 3Nk \left(\frac{4}{3} - \frac{1}{2}x - \log x \right).$$

This expression appears to be incorrect, in consequence of the omission of a term in the expansion of $\log(1 - e^{-x})$.

It is known that (Bernoulli's series)

$$\frac{1}{e^\xi - 1} = \frac{1}{\xi} - \frac{1}{2} + \frac{B_1 \xi}{2!} - \frac{B_2 \xi^2}{4!} + \dots \quad (-1)^{n-1} \frac{B_n}{(2n)!} \xi^{2n-1} \dots$$

where $B_1 = \frac{1}{6}$, $B_2 = \frac{1}{30}$, &c.

The series is convergent for values of the variable which are (numerically) less than 2π .

Now
$$\frac{d}{d\xi} \log(1 - e^{-\xi}) = \frac{1}{e^\xi - 1}.$$

Hence, by integration,

$$\log(1 - e^{-\xi}) = \log \xi - \frac{\xi}{2} + \frac{B_1 \xi^2}{2!} - \frac{B_2 \xi^4}{4!} + \dots \quad (-1)^{n-1} \frac{B_n}{(2n)!} \frac{\xi^{2n}}{2n} \dots$$

Again,

$$\begin{aligned} \int_0^x \frac{\xi^3 d\xi}{e^\xi - 1} &= \int_0^x \left(\xi^2 - \frac{\xi^3}{2} + \frac{B_1 \xi^4}{2!} - \frac{B_2 \xi^6}{4!} + \dots \quad (-1)^{n-1} \frac{B_n}{(2n)!} \xi^{2n+2} \dots \right) d\xi \\ &= \frac{x^3}{3} - \frac{x^4}{8} + \frac{B_1 x^5}{2! \cdot 5} - \frac{B_2 x^7}{4! \cdot 7} + \dots \quad (-1)^{n-1} \frac{B_n}{(2n)!} \frac{x^{2n+3}}{2n+3} \dots \end{aligned}$$

$$\text{Hence, } S_N = 3Nk \left\{ \frac{4}{3} - \frac{x}{2} + \frac{4B_1}{2!} \frac{x^2}{5} \dots + (-1)^{n-1} \frac{B_n}{(2n)!} \frac{4x^{2n}}{2n+3} \dots \right. \\ \left. - \log x + \frac{x}{2} - \frac{B_1}{2!} \frac{x^2}{2} \dots - (-1)^{n-1} \frac{B_n}{(2n)!} \frac{x^{2n}}{2n} \dots \right\}.$$

Thus the term in x disappears from the expansion, and in place of Ratnowsky's result we have

$$S_N = 3Nk \left\{ \frac{4}{3} - \log x + \frac{x^2}{40} \dots \right\},$$

or, approximately,

$$S_N = 3Nk \left\{ \frac{4}{3} - \log x \right\}.$$

§4. Assuming, with Ratnowsky, that the entropy of the liquid state can be calculated in the same way, and using accented letters for the liquid,

$$S'_N = 3Nk \left\{ \frac{4}{3} - \log x' \right\}.$$

The atomic heat of fusion, ρ , is equal to the difference of the entropies multiplied by the temperature of the melting point, T_s , or

$$\rho = T_s (S'_N - S_N).$$

Hence,

$$\rho = 3NkT_s \log \frac{x}{x'}.$$

Introducing the characteristic temperatures, θ , θ' defined by

$$\theta = h\nu_m/k, \quad \theta' = h\nu'_m/k,$$

$$\rho = 3NkT_s \log \frac{\theta}{\theta'}.$$

§5. Ratnowsky, taking the values of the atomic heat of fusion determined experimentally, calculated the values of θ/θ' by his formula for a number of metals, and came to the conclusion that θ/θ' is approximately constant for these cases. I have recalculated the values of the ratio by the formula above for the metals considered in my first Paper, and all the results are collected for comparison in the table. It will be seen that the values of θ/θ' in the last column are far from constant, varying from about 1.38 in the case of the alkali metals, to 2.52 in the case of bismuth.

Values of θ/θ' for the Metals.

Metal.	Ratnowsky.	Allen.
Cæsium	—	1.371
Rubidium.....	1.29	1.376
Sodium	1.31	1.379
Potassium.....	1.30	1.381
Iron.....	—	1.415
Silver.....	1.32	1.417
Lead	1.33	1.421
Copper.....	1.36	1.454
Palladium.....	1.40	1.499
Aluminium.....	1.39	1.530
Mercury	1.42	1.583
Cadmium	1.47	1.635
Platinum.....	—	1.645
Zinc	1.48	1.657
Tin.....	—	1.872
Gallium	—	2.300
Bismuth.....	—	2.519

A further objection to the conclusion of Ratnowsky may be put forward from a consideration of the case of mercury. The value of θ for the solid state calculated by the formula of Lindemann is about 66°K . (Ratnowsky gives 61°K .). The value of θ' for the liquid state may be calculated if we assume that the theory of Debye may be applied, since the compressibility of liquid mercury is known. This gives $\theta'=205^\circ\text{K}$., a temperature more than three times *higher* than that of the characteristic temperature of the solid state.

§6. It is to be noticed that the results tabulated by Ratnowsky for a number of chemical compounds in Tables II. to V. of his Paper are calculated by means of the formula

$$\rho = nNkT_s \log \frac{\theta}{\theta'},$$

which he regards as a rough approximation obtained by the omission of a term of the first order. Since it has been shown above that the terms of the first order disappear, his results in these cases may be regarded as accurate, and as showing an approximate constancy for the values of θ/θ' , assuming suitable values are taken for n , the number of degrees of freedom of a molecule. Since the value of n is somewhat arbitrarily chosen so as to secure a constant result, no secure conclusion can be drawn from the cases cited.

ABSTRACT.

A criticism is given of a theory of the process of fusion recently put forward by Ratnowsky. The author of the theory obtains an expression on certain assumptions for the entropy of a substance in

the solid state. He then proceeds to deduce a simple formula suitable for use at high temperatures. It is shown that this formula is incorrect in consequence of the omission of a term in the expansion. Assuming, with Ratnowsky, that the entropy of the liquid state can be calculated in the same way as that of the solid, a corrected expression is deduced for the atomic heat of fusion which is equal to the difference between the entropies multiplied by the temperature of the melting point. Ratnowsky, taking the values of the atomic heat of fusion determined experimentally, calculated the ratio of the "characteristic temperatures" for a number of metals, and came to the conclusion that the ratio is approximately constant. The values have been recalculated by the corrected formula, and it is found that they are far from constant. The ratio calculated for mercury by an independent method does not agree with the conclusion of Ratnowsky.

XXXI. *Cohesion (Second Paper).* By HERBERT CHATLEY, D.Sc. (Lond.).

RECEIVED MARCH 24, 1916.

Introduction.

It is very remarkable how little attention the subject of cohesion receives from students of physics. As far as the writer is aware, there is no standard text book which deals with the matter in any but the briefest way, and it is rarely that any suggestions are made which would link it with the theory of elasticity. The principal references in recent years are by Dewar ("Encyclopædia Britannica," art. "Liquid Gases"), Nernst ("Theory of the Solid State," London Univ. Press), and Pictet ("Les Basses Températures," Jnl. Roy. Soc. Arts, May 19, 1911). Curiously enough all three approach it from the same point of view—*i.e.*, low temperature phenomena. Dewar makes no suggestions as to rationale, beyond a tacit endorsement of Kelvin's gravitational theory; Nernst identifies cohesive force with chemical affinity on the basis of the fact that Schonflies proved the possibility of building up crystals from the molecular lattices. Pictet adheres to his old hypothesis of ether atmospheres about the atoms, and regards cohesion as the gravitational effect of atom on atom, subject to the limitation imposed by the ether cushion, which is merely strongly attracted by the atom. Zenner in the introduction to his "Technical Thermodynamics," abandons the Redtenbacher-Pictet theory, which he had previously adopted, but does not absolutely condemn it. Pictet distinguishes cohesion from chemical affinity, although asserting their specific unity, by supposing that the latter only operates (in a manner somewhat analogous to organic fertilisation of the ovum) when by thermal oscillations the propinquity of the material atomic centres is increased, the "ether atmosphere" which he postulates being burst through. In terms of the electron theory it may, perhaps, be supposed that elastic repulsion is due to the electrical repulsion between contiguous electron fields, but it is somewhat difficult to see how neutral atoms cohere under purely electrical conditions in virtue of electrical force only. Nevertheless, as mentioned below, cohesion seems to be comparable in magnitude with electrostatic force. To render the theory complete it is necessary to visualise an atom complex which:—

1. Attracts a dissimilarly charged atom with the full value corresponding to the charge and distance.

2. Attracts, when neutral, other neutral atoms with a force not incomparably small compared with electrostatic force. (A question here arises whether dissociated atoms do cohere in the strict sense of the word, or if they do not form molecules first.)

3. Attracts, neutral or charged, all other atoms, neutral or charged, with a force varying according to the Newtonian law at distances more than a few microns.

It would appear that molecular physics has or should have advanced to such a stage that this problem should not much longer remain unsolved.

Empirical Equations for Cohesive Force.

In a Paper read before the Physical Society in 1915 (Proc. Phys. Soc., Vol. XXVII., Pt. V., pp. 443-460, Aug. 15, 1915) the author suggested that certain empirical formulæ could be employed for the force between molecules known as cohesion. It is the object of this Paper to extend the subject and discuss various correlated facts and theories.

The principal formula suggested was as follows :—

Cohesion = attraction — repulsion,

$$t = k_2 d^{-\gamma_2} - k_1 d^{-\gamma_1},$$

where t is the cohesive bond between two molecules, d is the distance between the centres of the molecules, $k_1, k_2, \gamma_1, \gamma_2$ are coefficients. k_1 and k_2 vary with the substance, k_1 (if not k_2 also) increases with temperature. All are functions of d , but within small limits may probably be regarded as constants.

The following special cases occur :—

1. *Normal Equilibrium (solid)*—

$$t=0, k_2 d_0^{-\gamma_2} = k_1 d_0^{-\gamma_1}. \quad (d_0 = \text{normal molecular interval.})$$

2. *Elastic Strain of Small Amount*—

$\gamma_1 k_1 d_0^{-(\gamma_1+1)} - \gamma_2 k_2 d_0^{-(\gamma_2+1)} = E$. E is the modulus of elasticity in molecular terms (tension per molecule pair ÷ strain).

3. *Maximum Stress*.—

$$t_{\max.} = k_2 (c d_0)^{-\gamma_2} - k_1 (c d_0)^{-\gamma_1},$$

or,

$$\gamma_1 k_1 c^{-\gamma_1} d_0^{-(\gamma_1+1)} - \gamma_2 k_2 c^{-\gamma_2} d_0^{-(\gamma_2+1)} = 0.$$

c = ratio of extension under maximum (stable) stress.

4. *Liquefaction*—

$$-a = k_2(c_1 d_0)^{-\gamma_2} - m k_1(c_1 d_0)^{-\gamma_1}.$$

a =atmospheric pressure per molecule pair in direction of bond, c_1 =coefficient of expansion at temperature of liquefaction, m =ratio of coefficient k at this temperature to that at normal temperature.

5. *Pure Compression*—

$$-t = k_2 d^{-\gamma_2} - k_1 d^{-\gamma_1},$$

which must be negative, and equal to ∞ when $d=0$.

There are several difficulties in the way of evaluating the various coefficients in the above equations, but some useful values can be obtained by trial. Thus, if c is taken as 1.2, and $k_2=k_1$, $\gamma_2=4$, and $\gamma_1=5$, curves are obtained which closely resemble the stress-strain curves of metals. ($\gamma_1 > \gamma_2$ necessarily. *V. loc. cit.*)

A further condition when d is at least $>2d_0$, and may be as much as $5d_0$, is that the only remaining force (in the absence of a specially induced electric charge) is that of gravity, so that then

$$t = k_2 d^{-\gamma_2} = G m_1 m_2 d^{-2},$$

the usual Newtonian rule, which makes $k_2 = G m_1 m_2$ and $\gamma_2=2$.

Magnitude of the Attraction.

Kelvin opined that gravitation, as ordinarily understood, was competent to explain cohesive attractions. In the above-mentioned Paper the writer has examined this hypothesis, and finds it apparently incompatible with known molecular spacing.

Neglecting the repulsion (whose effect is, of course, to make the attraction less than it really is) a formula may be written

$$t = k_2 d^{-\gamma_2}.$$

Taking the case of iron, and *assuming* that in a simple tension the cohesive strength is simply due to the bonds between molecular couples in the direction of the stress, we may write approximately

$$t = \frac{981f}{n^2}.$$

t =attraction per molecule pair in dynes.

f =total tension, grammes per square centimetre, say, 2×10^6 ,
at ultimate stress.

n =molecules per centimetre length, say, 10^8 .

Write $981=10^3$, $t=2\times 10^{-7}$ dynes.

d is obviously $1/n$, say, 10^{-8} cm.

Then $2\times 10^{-7}=k_2(10^{-8})^{-\gamma_2}=k_2 10^{8\gamma_2}$,

and $k_2=2\times 10^{-7-8\gamma_2}$.

If $\gamma_2=2$, then $k_2=2\times 10^{-23}$,

and using the Newtonian form,

$$k_2=G_2m_1m_2=G_2m^2,$$

where m is the mass per molecule. Let σ =specific gravity,

$$m=\frac{\sigma}{n^3}=\sigma d^3, \text{ and } m^2=\sigma^2 d^6.$$

Writing for iron $\sigma=8$, and $d=10^{-8}$, as before,

$$G_2=\frac{k_2}{m_2}=\frac{2\times 10^{-23}}{64\times 10^{-48}}=3.0\times 10^{23}.$$

The ordinary molar value of G , the gravitation constant, is 6.6×10^{-8} , so that

$$\frac{G_2}{G}=\frac{3\times 10^{23}}{6.6\times 10^{-8}} \text{ approx. } 0.5\times 10^{31},$$

i.e., at molecular distances the "gravitational" force is increased about 10^{30} times.

It is interesting to note that this ratio is about the same as that of the *electrostatic* and gravitational attractions of two atoms.

The charge on an electron being 3.4×10^{-10} electrostatic units, the repulsion between two electrons at 1 cm. apart is 10^{-19} dynes and between one iron atom (carrying one free electron) and another (lacking one electron) the force is presumably the same.

The gravitational attraction between two iron atoms at 1 cm. apart is

$$\frac{6.6\times 10^{-8}\times 56^2}{10^{48}}=\text{approx. } 2\times 10^{-52} \text{ dynes,}$$

so that the ratio

$$\frac{\text{Electrostatic attraction}}{\text{Gravitational attraction}}=\frac{10^{-19}}{2\times 10^{-52}}=0.5\times 10^{33}.$$

Considering the very rough character of these computations, the agreement is quite close, and seems to indicate that the force of cohesion is comparable with the electrostatic forces between atoms—*i.e.*, chemical affinity.

Nernst and Lindemann are of this opinion (Nernst, "Theory of the Solid State," p. 4), but allege other reasons.

The alternative method of expressing the space variation by varying γ_2 is, perhaps, more logical mathematically, but does not touch on the rationale of the process, unless some such hypothesis as Crehore's ("Electrical World," 1912) is adopted. In this case, as the author has shown (*loc. cit.*, p. 448), a value $\gamma_2=6$ nearly fits the circumstances.

The Nature of Cohesive Force.

There is a general agreement that cohesive force is inferior in intensity to chemical affinity. The formulæ given above indicate a ratio

$$\frac{0.5 \times 10^{31}}{0.5 \times 10^{33}} = 10^{-2},$$

but there is, of course, no accuracy in a result obtained by such approximate methods.

Very great pressure even up to the elastic limit does not bring two smooth steel surfaces into such close contact that they cohere. This may, perhaps, be due to the presence of a film of air, and it would be interesting to find what degree of cohesion, over and above that due to air pressure, could be produced with surfaces of different degrees of smoothness pressed together *in a vacuum*.

When in a plastic (semi-liquid) condition, materials cohere under small pressure. An analogous fact is the smaller amount of tensile strength under such conditions. Lindemann believes that liquefaction occurs when the amplitude of the molecular oscillations is about the same as the molecular interval. If so, in a partially liquid substance, many of the surface molecules rise and fall to a relatively great extent, and presumably two plastic surfaces brought together cohere by reason of the very close proximity of the molecules during their ascents from the respective surfaces.

(An interesting and possibly useful speculation arising out of Lindemann's hypothesis is that dissociation occurs when the molecular frequency synchronises with the atomic frequency.)

The range of cohesion is very small (as has been shown experimentally by Quincke), since the force diminishes from great (tensile) values in solid to very small ones * in liquids

* Really negative ones, since the liquid is only maintained by air pressure.

with only small change of volume, and becomes less than zero in gases even under such great pressure that the volume is comparable (say, 10 times greater) with that of the liquid. The deviations from Boyle's law at high pressures, apart from Van der Waal's correction for the volume of the molecules, may perhaps have some cohesive relation, but the effect, if any, is excessively minute.

The average liquid occupies only a slightly larger volume than the solid from which it is produced, so that a very minute increase in the molecular interval causes an enormous reduction in the cohesive force. It must not, however, be forgotten that this is partially due to a great increase in the repulsive factor, but the fact of fracture in solids without very great extension indicates the simultaneous decrease of the attraction. The cases of ice and iron which contract during liquefaction may perhaps be due to chemical change. Ice, for instance, is believed to have the formula $2(\text{H}_2\text{O})$ (Nernst, "Solid State," p. 91), whereas water *may* be H_2O . If so, the more complex molecule probably has a smaller density, so that we may *suppose* that at the critical temperature of maximum density "liquid ice" becomes "water," or that from the commencement of liquefaction to 4°C . there is a gradual change in the proportions of ice and water. Presumably such a chemical change would have some distinct thermal or electrical effect.

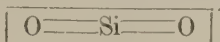
Cohesion can be effective in any direction about a particle, since amorphous solids exist, but the fact of crystallisation shows that it has directional variation—*i.e.*, it is a vector quantity. Chemical affinity is obviously a vector quantity as stereotomy shows, but the angular rate of change of the force must be immensely greater in the case of chemical attraction, since no amount of internal friction seems able to resist the formation of the atomic lattices termed molecules. Presumably the enormous electrostatic forces which exist around free atoms are not wholly neutralised in the formation of molecules, and cohesion is due to what electricians call "stray field."

If each atom be envisaged as a charged sphere enveloped in a dielectric (like Redtenbacher and Pictet's "Ether Atmospheres," which correspond to Thomson's electron fields about the positive core), then groups of such can be conceived, charged in various combinations, forming stable geometrical systems (the molecules). Such systems roughly aggregated would cohere by reason of stray field (amorphous solids), or if allowed to form slowly under conditions of maximum freedom

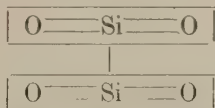
would establish configurations of maximum stability (crystals). There is a strong suggestion of the "three body" problem of astronomy in a still more complex form.

The outstanding difference between chemical affinity and cohesion lies in the selective character of the first. As far as the valency bonds of an atom being able to hold a molecule is concerned this is a common feature in organic compounds. What is distinct in the selective process is the feature of "saturation." Consider the case of silica $(\text{SiO}_2)_2$.

1. In each sub-molecule, the four valency bonds of the silicon atom are linked in pairs to two oxygen atoms, according to the stereotomic formula. This is purely chemical.



2. The sub-molecules are linked in pairs, if Nernst's formula $(\text{SiO}_2)_2$ is correct, thus :—



This is chemical in so far as it occurs in constant proportions, but is cohesive in so far as it is the linkage of molecules as distinct from atoms.

3. The silica molecules are linked to one another irrespective of quantity, but with a configuration of maximum stability (crystal) with four axes (hexagonal system). Linkage can occur without geometrical form (amorphous solid). The magnitude of the linkage forces is inferior to that of (1) and (2), but not incomparable (cohesion).

4. If gravitation is not a particular case of cohesion, then, in addition there is a small mutual attraction with no vector quality in accordance with Newton's law.

There is probably some relation between the number of atoms per molecule, and the system of crystallisation. Thus, $(\text{H}_2\text{O})_2$ and $(\text{SiO}_2)_2$ both contain 6 (or 3) atoms per molecule, and crystallise according to a hexagonal system.

Schonflies claims to have proved the possibility of building crystals up from molecules in an analogous manner.

It would seem possible to deduce from the fields about different stable systems of differently charged spheres some idea as to the feasibility or otherwise of explaining cohesion on these lines.

Relation of Frequency to Temperature in a Solid.

From formula in "Cohesion" (p. 444).

$$f = \frac{\sqrt{Js\theta}}{\pi\Delta}.$$

Write $\Delta = \Delta_0[1+m\theta]$.

Δ_0 = molecular interval at abs. zero.

$$f = \frac{\sqrt{Js\theta}}{\pi\Delta_0[1+m\theta]} ; J = 4.2 \times 10^7.$$

Example—

Iron : $s = 0.11$,

$$f = \frac{684.1\sqrt{\theta}}{\Delta_0[1+m\theta]}.$$

If $\theta = 900^\circ\text{C. abs.}$

$$f = \frac{20523}{\Delta_0[1+0.01]}.$$

Taking

$$\Delta_0 = 10^{-8},$$

$$f = 2.0 \times 10^{12} \text{ at } 900^\circ\text{C. abs.}$$

and

$$0.5 \times 10^{12} \text{ at } 450^\circ\text{C. abs.}$$

or, if

$$f = 4.0 \times 10^{14} \text{ at } 900^\circ\text{C. abs. (See "Cohesion," p. 445.)}$$

sion," p. 445.)

$$\Delta_0 = 0.5 \times 10^{-10}.$$

(Note.—Clerical error on p. 445, 0.5×10^{-8} should be 0.5×10^{-10} . Either the radiation frequency exceeds the molecular frequency as calculated above or the molecular interval is much less.)

Generally, if $\Delta_0 = 10^{-8}$,

$$f = \frac{684\sqrt{\theta}}{10^{-8}[1+m\theta]} = \text{say, } 7 \times 10^{10}\sqrt{\theta}.$$

Cf. Lindemann's formula (Nernst, p. 49) for atomic frequency.

$f = 3.08 \times 10^{12} \sqrt{\frac{T_s}{mv^{2/3}}}$ = from 1 to 50 times 10^{12} for most monatomic solids (for monatomic solids), where T_s is melting temperature, v is vol. in cubic centimetres of m grammes, m is atomic weight.

DISCUSSION.

Dr. H. S. ALLEN (communicated): The nature of the attractive force producing cohesion and rigidity has been discussed by several writers, including Sutherland,* who attributes the attraction to electrostatic forces arising from electric doublets, and A. P. Mathews.† The latter writer suggests that molecular cohesion may be due to magnetic forces. "Is it not possible that molecular cohesion, involving, as it does, both atomic and valence electrons (atomic weight and valence), is due, perhaps, to the magnetic effects produced by the movements of these electron couples? In this view the atoms would be united by their electrostatic affinities, and these same valences and the other atomic electrons by their magnetic effects produce the molecular cohesion." The difficulty attaching to this view appears to be the necessity for postulating very large magnetic moments for the molecules. "Weiss, who has considered the possibility of the identity of cohesion and magnetism, states that he will shortly show that they cannot be identical." It must be emphasised that in a crystalline solid, very intense *local* molecular fields must exist whatever may prove to be the nature of the cohesive forces. An interesting illustration of quasi-rigidity imparted to an assemblage of independent bodies by the application of a magnetic field, is afforded by a handful of small iron nails or tacks thrown between the poles of a strong electromagnet. The nails arrange themselves in chains or bridges between the poles, such chains offering considerable resistance to distortion. If the nails are sufficiently numerous they form a compact mass between the magnet poles which can be broken only by the application of a large force. In such a case the *local* forces predominate. This has been emphasised by Larmor‡ and by Oxley.§ "If we suspend a bunch of iron nails from the pole of a magnet, we find that they adhere to each other end-wise, and repel one another sideways, while non-adjacent nails have no action on one another." Thus modifications in the values of the forces are necessitated "by the recognition of the discrete or molecular character of the polarised elements." Amorphous solids may be regarded as supercooled liquids. Even in a liquid the force of cohesion may be considerable, as is shown by the comparatively large value the tensile stress may attain. The important point in Prof. Chatley's Papers appears to be the clear recognition of the fact that it is necessary to consider both an attractive and a repulsive force between the molecules. It may be mentioned that in 1903 Mie|| advanced a theory of monatomic solid bodies characterised by the assumption that the atoms are constrained in definite equilibrium positions by attractive and repulsive forces between them. The same hypothesis was afterwards employed by Grüneisen¶ and by Ratnowsky** in the development of an equation of state for solid bodies.

* See especially "The Electric Origin of Rigidity," "Phil. Mag.," Vol. VII., p. 417, 1904.

† "Journal" of Physical Chemistry, Vol. XVII., p. 481, 1913.

‡ Larmor, "Proc." Roy. Soc., A, Vol. LII., p. 64, 1892.

§ Oxley, "Phil. Trans." Roy. Soc., A, Vol. CCXV., p. 91, 1914.

|| "Ann. d. Phys.," Vol. XI., p. 657, 1903.

¶ "Physik. Zeitschr.," Vol. XII., p. 1023, 1911.

** "Ann. d. Phys.," Vol. XXXVIII. p. 637, 1912.

XXXII. *On the Significance of Ionic Migration Experiments.*
 By DR. S. W. J. SMITH, F.R.S.

RECEIVED JULY 18, 1916.

1. *Migration Data for Copper Sulphate Solutions.*—The results presented in the Paper read recently before the Physical Society by Mrs. C. H. Griffiths* are such that, as I pointed out at the time,† they are not likely to be accepted without question by those who have been accustomed to regard Hittorf's fundamental measurements, of the migration constant for copper sulphate, as certainly correct "within one or two units in the second decimal place."

The values obtained for this constant by Mrs. Griffiths are uniformly higher than those of Hittorf. For the concentrated solutions the difference is relatively small. It is not much greater than the amount by which Hittorf's results may be in error. The difference increases with dilution until it amounts to four or five units in the second place, and there is no sign that it would not have become greater still if the dilution had been carried as far as it was by Hittorf.

For well-known reasons, the properties of dilute solutions have been the subject of careful study and the migration constant of such solutions has not escaped attention. The experiments upon which the greatest reliance has been placed—*e.g.*, those of Bein‡—have tended to confirm the substantial correctness of Hittorf's numbers in this region. The experiments of Kirmis, as he himself remarked,§ seemed to show that, for concentrated and for dilute solutions alike, the results are not seriously in error. The experiments of Metelka are not exactly comparable with those of Hittorf; but, except in one solution, they agree with his. The same is true of some of Wiedemann's results and also of isolated experiments by Gordon|| and by Hopfgartner,¶ within the limits already mentioned. The difference between Hittorf's results and those obtained by Mrs. Griffiths is the more striking in that the appa-

* "Proc." Phys. Soc., 28, p. 132, 1916.

† "Bulletin" Phys. Soc., 1916, p. 24.

‡ "Wied. Ann.," 46, p. 29, 1892; "Zeits. Physik. Chem.," 27, p. 1, 1898.

§ "Wied. Ann.," 4, p. 507, 1878.

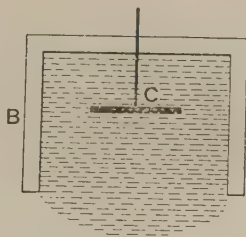
|| "Zeits. f. Physik. Chem.," 23, p. 469, 1897.

¶ *Ibid.*, Vol. 25, p. 115.

ratus used by her resembles the original apparatus* more closely in some ways than any of the various devices which have been used to test or to improve upon Hittorf's measurements. In both the cathode vessel is a vertical cylinder closed at the top, and the measurements depend, in closely related ways, upon what happens within this vessel during the course of the experiment.

2. *Two Methods of Applying Hittorf's Principle.*—The relation between the two methods may be expressed in the following way, neglecting at first certain necessary qualifications which will be considered afterwards.

Imagine a solution of copper sulphate, from which copper can be deposited upon a cathode, C, to be contained within a cathode vessel B, as shown diagrammatically in the Figure below.



Let the weights of the Cu and SO_4 ions (in gms.) be represented by c and a respectively, and let u/v represent the ratio of the velocities of these ions under the same potential gradient. Then, during the deposition of $(u+v)c$ gms. of Cu upon C, $v(a+c)$ gms. of Cu SO_4 will leave the liquid round the cathode, va gms. SO_4 will leave the cathode vessel and uc gms. Cu will enter it.

If we denote the loss in weight of the cathode vessel by l , the loss of Cu SO_4 by l' and the weight of copper deposited by w , we find at once that—

$$\frac{l'}{w} = \frac{v}{u+v} \cdot \frac{a+c}{c} = \frac{l}{w} + 1.$$

And if we write $v/(u+v) = n$,

we get
$$n = \frac{c}{a+c} \cdot \frac{l'}{w} = \frac{c}{a+c} \cdot \left(\frac{l}{w} + 1 \right).$$

* "Pogg. Ann.," 89, p. 187, 1853.

Hence, if we measure either l'/w or l/w we can determine n , the value of $c/(a+c)$ being equal to $1/2.511$, very nearly, when modern atomic weights are used.

Hittorf measured l' directly (being able to isolate the cathode vessel for this purpose), while Mrs. Griffiths has measured l .^{*} Hittorf, for reasons which he gives, deduced the values of w from the weights of silver deposited in a voltameter in series with the migration vessel; but, except for the weaker solutions, he also measured w directly—the copper being deposited upon a (silver) cathode of a shape to which reference is made later on. The values of w , obtained directly and indirectly, were usually the same within a few parts per thousand. Mrs. Griffiths deduces the value of w from the current, the time it is passed and the electrochemical equivalent of copper.

The fact that Mrs. Griffiths, in addition, measured the current density and hence, knowing the concentration of the solution, the electrochemical equivalent of copper and its atomic weight, calculated u and v separately (really au and av , where a is the coefficient of ionisation) does not constitute an essential difference between the methods. The value of $a(u_0+v_0)$ can be calculated for any solution of which the conductivity and molecular concentration are known and hence, from measurements by Hittorf's method, the separate values of au_0 and av_0 can be determined. Here u_0 and v_0 refer to the ionic velocities under unit potential gradient. The values of au and av given by Mrs. Griffiths correspond with undetermined potential gradients, since the conductivities of the solutions employed were not obtained. Similar calculations could, if desired, be made from Hittorf's data, since he also gives the diameter of his cathode vessel; but, as a matter of fact, the validity of this method of measuring ionic velocities is now doubtful because, if the ions are hydrated, as seems to be the case in general, the migration constant n can only accidentally be equal to $v/(u+v)$ in solutions of moderate concentration.

3. *Disturbing Factors.*—Before proceeding further it is necessary to remove the imperfections from the sketch, given above, of the two different methods of applying Hittorf's principle.

There are at least two disturbing factors, recognised by Mrs. Griffiths, of which Hittorf was fully aware.[†] In the first place

^{*} By suspending the cathode vessel from the pan of a balance.

[†] *L.c.*, p. 197.

the copper deposited on the cathode reduces the volume of the cathode vessel and so tends to expel some of the solution. In the second, the disappearance of Cu SO_4 from the cathode region is accompanied by a decrease in the volume of the solution from which it is removed. This tends to cause some of the surrounding liquid to enter the cathode vessel. The volume of liquid which the deposited copper tends to expel is obviously w/d , where d is the density of the copper deposited under the conditions of the experiment (to which Hittorf ascribes the value 8.914 obtained by Marchand and Scheerer). To set against this we have the volume which tends to enter and which, as Hittorf points out, it is impossible to estimate exactly. The reason for this is that we do not know exactly how the loss of salt is, as it were, distributed over the water which remains.

Suppose the original solution to be of density ρ , and to contain β gms. of Cu SO_4 per unit weight. (Hittorf gives both of these quantities for the solutions which he used.) Suppose further that the loss of salt, l' , is distributed over a certain mass, W , of the water above the cathode and let this water (at the end of the experiment) give with the Cu SO_4 which it contains a solution of density ρ' containing β' gms. Cu SO_4 per unit weight. The initial volume of this solution was $W/\rho(1-\beta)$. The final volume is $W/\rho'(1-\beta')$. The contraction is, therefore,

$$W\{1/\rho(1-\beta) - 1/\rho'(1-\beta')\}.$$

We have also $l' = W\{\beta/(1-\beta) - \beta'/(1-\beta')\}$.

Whence the contraction is—

$$l' \cdot \frac{1/\rho(1-\beta) - 1/\rho'(1-\beta')}{\beta/(1-\beta) - \beta'/(1-\beta')}.$$

The values of ρ and β are determined by the concentration of the solution used in the experiment, but the values of ρ' and β' , for a given value of l' , depend upon the assumed magnitude of W . The maximum value of W is obviously the whole mass of water round and above the cathode in the cathode vessel. In that case the values of ρ' and β' will also be the largest possible for a given value of l' . It happens at the same time, for most solutions of Cu SO_4 at any rate, that the contraction for a given loss of salt will be greatest when the loss is distributed as uniformly as possible over the whole of the water above the cathode.

If, on the other hand, the loss is restricted as much as possible in its distribution, for example so that a certain mass of water is deprived of the whole of its salt content while the rest contains the original percentage of salt, then the change in volume for a given loss of salt will be relatively small. Its value will be $l' \{1 - \rho(1 - \beta)\} / \beta\rho$.

4 *Their Influence in Hittorf's Method.*—The actual contraction in any given case will be somewhere between these two extremes, being nearer the one or the other according as the mixing of the different elements of the cathode solution is more or less complete.

It will be sufficient for the moment to assume that the contraction can be represented by $l'\delta$. The net amount of Cu SO_4 lost by the cathode vessel during the experiment, in consequence of the two disturbing factors, will then be—

$$\left\{ \frac{w}{d} - \frac{a+c}{c} n w \delta \right\} \beta \rho.$$

Hence the corrected expression for l' , the total loss of Cu SO_4 by the cathode vessel during the experiment, is—

$$l' = w \left\{ n \cdot \frac{a+c}{c} (1 - \beta \delta \rho) + \frac{\beta \rho}{d} \right\},$$

whence
$$n = \frac{c}{a+c} \cdot \frac{l' / w - \beta \rho / d}{1 - \beta \delta \rho} \quad \dots \dots \dots \text{(H.)}$$

If we write this equation in the form

$$n = \frac{c}{a+c} \cdot \frac{l'}{w} \cdot \left\{ 1 - \frac{\beta \rho (w / l' d - \delta)}{1 - \beta \delta \rho} \right\},$$

we see at once that the simple theory of Hittorf's method will lead to appreciable error unless either

$$\text{(i.)} \quad w / l' d - \delta = 0$$

$$\text{or (ii.)} \quad \frac{\beta \rho (w / l' d - \delta)}{1 - \beta \delta \rho}$$

is small in comparison with unity.

5. *Estimation of Possible Errors.*—With respect to (i.) above, it happens, curiously enough, that, in dilute solutions of Cu SO_4 , $w / l' d$ can be greater than δ , while in concentrated solutions the converse is true. Hence, subject to the limitations imposed by uncertainty in the value of δ in any particular case, there should be solutions for which the simple theory is almost

exactly sufficient. Such solutions are those of which the density lies somewhere near 1.05.* In more dilute solutions the uncorrected n would be too large, in more concentrated solutions too small.

The condition (ii.) is, however, of more general interest. From what has just been said, it will be seen that, in order to discover the maximum error in n , caused by neglect of volume changes, it is enough to consider the case of the most concentrated solution used. For, on account of the factor β , the quantity $\beta\rho(w/l'd - \delta)/(1 - \beta\delta\rho)$ will always be much smaller in very dilute than in concentrated solutions.

The strongest solution used by Hittorf had a density of about 1.15 ($\beta=0.136$). For this the value of $w/l'd$ was approximately 0.06 and that of $\beta\rho$ approximately 0.16. Hence we may put

$$n=n'\{1-0.16(0.06-\delta)\},$$

where n' is the uncorrected value of n . In order to estimate δ , Hittorf assumed that the cathode loss could be considered to result in the substitution, for a certain quantity of the original solution, of a quantity, containing the same amount of water, of the second solution which he used. He knew the values of ρ' (about 1.10) and β' (about 0.095) for this solution and hence deduced a value for δ . It was approximately 0.07. In that case, we should have $n=n'\times 1.0016$, or the uncorrected value of n would be about 1.5 parts per 1,000 too small. Since the unavoidable errors of experiment were greater than this, Hittorf concluded that the correction was superfluous.

If Hittorf had assumed the loss to consist in the removal of the whole of the salt from a given mass of the solution, leaving the rest unchanged, the value of δ would have been approximately 0.03. In this extreme case (against which diffusion would operate effectually) n' would be too large, but would still be within 0.5 per cent. of the true value.

If, on the other hand, we make use of the tables compiled by Gerlach† from data given earlier by Schiff‡ (as, apparently, Mrs. Griffiths has done), we can estimate the limiting value of δ in the other direction, *i.e.*, when we suppose the loss shared equally by the whole of the liquid above the cathode. The value of δ would then be about 0.11 and, in this case, n' would

* Assuming the values of δ given by Mrs. Griffiths to be approximately correct.

† "Zeits. Analyt. Chem.," 8, p. 288, 1869.

‡ "Ann. Chem. Pharm.," 110, p. 71, 1859.

be about 0.8 per cent. too small. Such a correction would bring Hittorf's higher values considerably nearer to those of Mrs. Griffiths.

When estimating the reliability of Hittorf's results, it must not be forgotten, however, that in later experiments* the disturbing factors here considered were avoided.

The calculation of the cathode loss was not based upon the volume of the liquid contained by the cathode vessel after the experiment, but upon its weight. Thus, let w_1 be the weight of the solution in the cathode vessel after the experiment and w_2 the weight of Cu SO_4 (determined by analysis) which this solution contains. Then, if β be the weight of salt per unit weight of the original solution, the true cathode loss of salt is expressed by $l' = \beta(w_1 - w_2)/(1 - \beta) - w_2$, and the simple formula

$$n = \frac{c}{a+c} \cdot \frac{l'}{w} \text{ applies.}$$

The same expression holds good, with sign reversed, for the anode gain. The result obtained for the solution of specific gravity about 1.10, by this method, using the anode gain, was (as it should be) slightly larger than, but practically identical with, that previously obtained—viz., 0.716, compared with 0.713.†

6. *The Griffiths Method.*—In this method of measuring the migration constant, the loss of weight of the cathode vessel owing to migration is $\frac{a+c}{c}nw - w$. The loss due to the disturbing influences considered above is now

$$\left\{ \frac{w}{d} - \frac{a+c}{c}nw\delta \right\} \rho.$$

Hence the correct value for n , if l is the total loss in weight of the cathode vessel, is

$$n = \frac{c}{a+c} \cdot \frac{l/w + 1 - \rho/d}{1 - \delta\rho} \quad \dots \dots \dots (\text{G.})$$

If we write this in the form

$$n = \frac{c}{a+c} \cdot \left(\frac{l}{w} + 1 \right) \left\{ 1 - \frac{\rho(w/(l+w)d - \delta)}{1 - \delta\rho} \right\},$$

* "Pogg. Ann.," 98, p. 1, 1856.

† All Hittorf's results would be altered slightly by the substitution of modern atomic weights for those used by him.

we see that the simple theory of the method will lead to appreciable error, as in the other case, unless

$$\text{either (iii.)} \quad w/(l+w)d - \delta = 0$$

$$\text{or (iv.)} \quad \frac{\rho(w/(l+w)d - \delta)}{1 - \delta\rho}$$

is small in comparison with unity.

7. *Its Disadvantages Compared with Hittorf's Method.*—With respect to (iii.), as in the case of (i.), it will be found that the condition can apparently be satisfied when ρ is in the neighbourhood of 1.05. But comparing (iv.) with (ii.), it will be seen that the correction no longer decreases rapidly as the solutions become more and more dilute, and, even in the strongest solutions, is much greater than before. It follows that if there is any uncertainty as to the volume changes, already discussed, the second method will compare unfavourably with the first.

8. *Uncertainty in the Estimates of δ .*—The following numerical example will illustrate the uncertainty with respect to δ .

For the solution of density 1.0273, Mrs. Griffiths takes $\delta = 0.044(31)$, which is deducible from Gerlach's values,

$$\begin{aligned} \rho &= 1.1038, \beta = 0.03834 \\ \rho' &= 1.0254, \beta' = 0.02556, \end{aligned}$$

and obtains for n the value 0.6910, Hittorf's value for a similar solution lying between 0.645 and 0.65.

Inspection of Gerlach's data seems to show that they are not as accurate as Mrs. Griffiths supposes. Apart from this, there is the difficulty that the data given by Hittorf* (so far as they are comparable), by Kohlrausch† and by Archibald‡ lead to other values for δ . The results are not very consistent with one another, but tend to show that the value $\delta = 0.04$ is too high. Perhaps as much as 50 per cent. too high. Hence, even when the method of allowing for volume changes which Mrs. Griffiths adopts is assumed to be correct, the uncertainty of the data upon which she relies is such that the value of n to which her own observations lead may be considerably less than 0.69.

* *L.c.*, p. 196, 1853.

† "Wied. Ann.," 6, p. 20, 1879.

‡ "Trans." Nov. Scot. Inst., Vol. IX., 1897, quoted in "Landolt-Börnstein-Roth Tabellen," 4 Aufl., p. 284, 1912.

9. *Uncertainty Concerning the Effective Density of the Cathode Deposit.*—The doubt concerning δ is not the only one. The value $d=8.952$, also taken from tables by Mrs. Griffiths, may be sufficiently near the true density of electrolytically deposited copper under normal circumstances; but there is always the danger that the amount of solution which the electrolytic processes tend to expel from the cathode vessel is greater than w/d . Small quantities of gas, such as hydrogen deposited with the copper, oxygen freed from solution by change in temperature or evolved at the anode, may collect in the cathode vessel. The effect of these will be practically equivalent to a reduction in d since their weight will be negligible. Hydrogen is the most probable source of error of this kind. It would tend to make the calculated value of n too large and, since it is most likely to be evolved from the weakest solutions, it is a possible cause of the main difference between the results obtained by the two methods. For, as in the case of δ , the first method is obviously affected much less than the second by changes in d .

It is interesting in this connection to recall the remarks made by Hittorf with respect to the shape which he chose for his cathode.* It consisted of a silver cone with axis vertical and apex downwards. A horizontal glass disc was fixed at its centre to the apex of this cone in order, as he explains, to obtain a nearly uniform deposit. The anode was a horizontal, perforated, disc; but, referring to the cathode, Hittorf says that if the latter is a horizontal plate the deposited metal is not adherent. He remarks also † that in dilute solutions (of density 1.025 or less) the copper was deposited, even on his cathode, in a spongy form and could not be weighed. A spongy deposit is a frequent precursor of hydrogen.

Mrs. Griffiths obtained a value for the electrochemical equivalent of copper, which was not more than one-third per cent. too small, by means of a cathode similar to that employed in the migration experiments. It might be inferred from this that the effect of hydrogen in the migration experiments was probably unimportant. It has to be remembered however, that, in the determination of the equivalent, the cathode was not enclosed. Apart from the fact that hydrogen which escaped would not materially affect the result in this case, it is obvious that efficient convection, which is all-important

* *L.c.*, p. 187.

† *L.c.*, p. 195.

if evolution of hydrogen is to be prevented, would be more likely to occur in this than in the migration experiment.

To sum up, we may say that the results obtained by the second method, ingenious as it is, cannot be accepted as superior to Hittorf's until it is shown that errors in the estimation of δ and of d , which can easily occur, have been avoided.

10. *Hydration and its Influence upon the Results obtained by the Two Methods.*—The possibility that the ions may be hydrated has already been mentioned; but has, so far, been ignored. It remains to enquire how this hydration would affect the significance of the results obtained by either method.

For this purpose we may suppose that the gm. ions of Cu and SO_4 carry with them, respectively, C and A gm. mols. of water. With this supposition we see that when $(u+v)c$ gms. of Cu are deposited, u gm. ions of Cu give up uC gm. mols. of water at the cathode, while v gm. ions of SO_4 carry vA gm. mols. away.

If, for definiteness, we assume $uC > vA$, it follows that $\frac{uC-vA}{(u+v)c}w$ gm. mols. of water are carried into the cathode space, for every w gms. of Cu deposited.

There is thus another possible source of dilution at the cathode. It will tend to increase the amount of solution expelled from the cathode vessel.

We may consider this effect to be superposed on that already dealt with. We shall then have to find how the volume of a solution containing a given mass M of salt is increased when the amount of water W , which it contains, is increased by a known quantity. Using the same symbols as before, we write

$$V = \frac{M}{\beta\rho} \text{ and } W = \frac{1-\beta}{\beta}M,$$

whence

$$\left(\frac{\partial V}{\partial W}\right)_M = \partial\left(\frac{1}{\beta\rho}\right) / \partial\left(\frac{1-\beta}{\beta}\right).$$

Following the previous plan we may write this in the form

$$\gamma = \frac{1/\beta\rho - 1/\beta'\rho'}{(1-\beta)/\beta - (1-\beta')/\beta'},$$

from which the value of γ for a solution of given density ρ can

be found in the same way and with the same limitations as was δ .*

Hence, if we denote the weight of a gm. mol. of water by g , the amount by which the volume of the cathode liquid is increased, when w gms. of Cu are deposited, is

$$\frac{uC-vA}{(u+v)c}wg\gamma,$$

and the complete expression for the volume of Cu SO₄ solution expelled from the cathode vessel should be

$$\left\{ \frac{w}{d} + \frac{uC-vA}{(u+v)c}gw\gamma - \frac{a+c}{c}nw\delta \right\}.$$

Hence the total loss of Cu SO₄ by the cathode vessel is $\frac{a+c}{c}nw$ plus the above quantity multiplied by $\beta\rho$.

Writing out the new expression for l' , and comparing it with that already found, it will be seen that we can deduce the equation

$$n = \frac{v}{u+v} = n_H - \frac{g}{a+c} \cdot \frac{\beta\gamma\rho}{1-\beta\delta\rho} \cdot \{(1-n)C-nA\},$$

where n_H is the value for n found by Hittorf's method when hydration is ignored.

Considering the plan adopted in the second method in the same way, it will be seen that the total loss in weight of the cathode vessel, owing to migration, is

$$\left\{ \frac{a+c}{c}nw - w \right\} - \frac{g}{c} \{(1-n)C-nA\}w,$$

while the amount of solution expelled owing to volume changes produced within the cathode region, is the same as in the first case.

Writing down the new expression for l , we can deduce the result

$$n = \frac{v}{u+v} = n_G - \frac{g}{a+c} \cdot \frac{\gamma\rho-1}{1-\delta\rho} \cdot \{(1-n)C-nA\},$$

where n_G is the value for n found by the Griffiths method when hydration is neglected.

* The corresponding equation for δ , obtained from $V = \frac{W}{\rho(1-\beta)}$ and $M = \frac{\beta}{1-\beta}W$, is $\left(\frac{V}{\partial M}\right)_W = \partial \left(\frac{1}{\rho(1-\beta)}\right) / \partial \left(\frac{\beta}{1-\beta}\right)$.

When this expression is compared with that containing n_H , it will be seen that the experimental values, n_G and n_H , will not coincide unless the values of

$$\frac{\beta\gamma\rho}{1-\beta\delta\rho} \text{ and } \frac{\gamma\rho-1}{1-\delta\rho}$$

are the same within the limits of experimental error.

The values of these quantities, for different values of ρ , can be determined if we assume Gerlach's tables to be sufficiently accurate. The following approximate table will serve to indicate how they vary with ρ :—

ρ	$\beta\gamma\rho/(1-\beta\delta\rho)$	$(\gamma\rho-1)/(1-\delta\rho)$
1.1083	0.116	0.115
1.0554	0.058	0.057
1.0273	0.028	0.028

They are thus practically identical when ρ is small, although, as ρ increases, the numbers in the second column increase rather more rapidly than those in the third. This means that n_H should increase slightly with respect to n_G as ρ increases. The actual difference for any value of ρ would be negligible unless the factor $\{(1-n)C-nA\}$ were large since $g/(a+c)$ is only 0.113. But, in any case, it is seen that hydration cannot be the cause of the difference between the results obtained by the two methods.

11. *The Variation in the Value of the Migration Constant.*—The data just given would enable us to calculate the true value of n from a series of values of the migration constant, using solutions of different strengths, if we could assume that the ratio of the ionic velocities and the degree of hydration of the ions were constant.

If, to test the validity of such assumptions, we take Mrs. Griffiths' values of n_G , we find that they appear to be fairly consistent with $n=0.675$. Similarly if, from Hittorf's measurements, we obtain corresponding values of n_H , we find that the value of n , which would satisfy Hittorf's results, would be approximately 0.625. This is Metelka's value for the migration constant in very dilute solutions, and, since in such solutions n_H and n should practically coincide, it might seem that u/v is, in fact, independent of the concentration, and that the degree of hydration of the ions is also constant.

This simple interpretation of the results does not, however,

agree with data obtained by Steele* using the moving boundary method of comparing ionic velocities. For a solution containing 1 gm. mol. of Cu SO_4 per litre he found $v/u=2.71$, whence $n=0.73$; while for a solution of half this strength he found $v/u=1.94$ or $n=0.66$. Therefore, if these results are correct, n is far from constant in the region of concentration to which they apply. Variations of this kind would complicate the theory of the experiments. Their most probable cause would be variations in C and in A . If, for simplicity, we assume the moving particles to be spherical, and to have volumes proportional to C and to A , an attempt to interpret the results can be made; but it would appear not to meet the present case. With dilute solutions, however, such hypotheses are apparently more successful†, and attempts have been made to deduce values of C and A in this region in which, probably, their variations are comparatively small.

12. *Comparisons of n_H with $n=v/(u+v)$.*—It would appear that dilute solutions of Cu SO_4 have not been examined by the direct method‡; but results have been published for other salts. In some of these the migration constant obtained by the Hittorf method is practically identical with the value of $v/(u+v)$ obtained directly. For example,§ in dilute NaCl , $n=u/(u+v)=0.617=n_H$.

The disturbing influence of hydration would, as the equations of §10 show, be relatively unimportant in dilute solutions. In more concentrated solutions, however, the value of

$$\frac{g}{a+c} \cdot \frac{\beta\gamma\rho}{1-\beta\delta\rho} \cdot \{(1-n)C-nA\}$$

might easily become appreciable. For a normal solution of Na Cl , Denison and Steele found $n=u/(u+v)=0.614$, while the Hittorf method had given $n_H=0.637$. The existence of such differences was verified repeatedly. It was not seen till later that they could be due to hydration. The most satisfactory evidence was supplied by Washburn.||

His method¶ can be presented in the following way: Suppose that a substance can be found which, when dissolved along with the electrolyte, does not move under the influence of the

* Phil. "Trans.," A, 198, p. 129, 1902.

† Cf. Riesenfeld and Reinhold, "Zeits. Physik. Chem.," 66, p. 682, 1909.

‡ Cf. Steele, *l.c.*, p. 122.

§ Denison and Steele, "Zeits. Physik. Chem.," 57, p. 117, 1907.

|| "Journ." Amer. Chem. Soc., 31, p. 353, 1909.

¶ Cf. Nernst, Garrard and Oppermann, "Gött. Nachr.," 56, p. 86, 1900.

potential gradient. Let the solution contain this substance in known amount, say, r gms. per cc. During the deposition of w gms. of metal, the volume of the solution expelled from the cathode vessel will be, as before,

$$w \left\{ \frac{1}{d} - \frac{a+c}{c} n\delta + \frac{uC-vA}{(u+v)c} g\gamma \right\}$$

if we suppose the volume changes to be unaffected by the presence of the non-electrolyte.

From this we get

$$\{(1-n)C-nA\} = \frac{c}{g\gamma} \left\{ \frac{l''}{wr} - \frac{1}{d} + \frac{a+c}{c} n\delta \right\},$$

where l'' is the mass of non-electrolyte lost by the cathode vessel during the migration experiment. Hence, if l'' be measured, the hydration factor can be determined when $\left(\frac{1}{d} - \frac{a+c}{c} n\delta\right)$ is known sufficiently accurately, or is, as sometimes happens, small enough to be neglected.

For a solution containing 1.25 gm. mols. of Na Cl per litre, Washburn found by Hittorf's method $n_H=0.634$, and from this, when the hydration factor was determined in the way indicated above, he obtained $n=v/(u+v)=0.617$.

More could be said concerning the interest* which is attached to the determination of migration constants, for example their relation to diffusion constants† has been left untouched; but I venture to hope that these Notes,‡ rather hurriedly written, and perhaps not free from numerical errors, may be of some general interest and may encourage Mrs. Griffiths to continue her work.

* Cf. Mrs. Griffiths, concluding paragraph, *l.c.*, p. 146.

† Cf., e.g., the diffusion data given by B. W. Clack, "Proc." Phys. Soc., 27, p. 63, 1914, with the corresponding migration data, Kohlrausch and Holborn, "Leitvermögen der Elektrolyte," p. 201, 1898.

‡ Which are a version of the contribution to the discussion on Mrs. Griffiths' Paper, referred to on p. 316.

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